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ON THE ANILIDES OF FUMARIC AND MALEIC ACIDS AND ON PHENYLASPARTIC ACID.[1]

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In the course of comparative researches, which have extended over a long period in this laboratory, on fumaric and maleic acids, itaconic, mesaconic and citraconic acids, O. Strecker prepared the amides and anilides of the three last-mentioned acids.[2] The investigation of the amides and anilides of fumaric and maleic acids ought to be pursued in connection with that of the transformation of both acid chlorides. The serious difficulties, however, which we have thus far encountered in attempts to obtain the chloride of maleic acid in a state of purity have prevented our efforts being crowned with success. If, notwithstanding this, we communicate our experience with the anilides of both acids, we are compelled to take this step on account of the extensive investigations which Michael has for some time been carrying on in the same field, the results of which do not harmonize with our observations. We will therefore give our results obtained in studying the anilides of fumaric and maleic acids together with the analytical proofs, and then compare the same with those of Michael and Wing[3] as well as those of Michael and Palmer.[4]

[1] Communicated by the Authors. [2] Ber. d. deutsch. chem. Ges. **15**, 1639.
[3] This Journal **7**, 280. [4] This Journal **9**, 197; and Ber. d. deutsch. chem. Ges. **19**, 1375.

Fumaric dianilide, $\begin{matrix}CH.CONH.C_6H_5\\ \|\\ CH.CONH.C_6H_5\end{matrix}$.—We prepared this compound by gradually mixing an ethereal solution of aniline and an ethereal solution of fumaryl chloride. On treatment with water, in which the fumaric dianilide is insoluble, it is separated from the aniline hydrochloride, which is also formed during the reaction. The dianilide is almost insoluble in ether, very difficultly soluble in alcohol and in glacial acetic acid. It crystallises from the latter in white microscopic needles, which turn brown at 275° without melting. When heated with a concentrated solution of alcoholic potash in a closed tube by means of a water-bath, the fumaric dianilide is decomposed into aniline and fumaric acid.

I. 0.1713 gram substance burned with chromate of lead gave 0.4490 gram CO_2 and 0.0867 gram H_2O.

II. 0.1946 gram substance burned in open tube gave 0.5124 gram CO_2 and 0.0999 gram H_2O.

III. 0.1397 gram substance burned in open tube gave 0.3678 gram CO_2 and 0.0696 gram H_2O.

IV. 0.3682 gram substance gave 34.6 cc. N at 24° and under 753.5 mm. pressure.

	Theory for $C_{16}H_{14}N_2O_2$.	Found.			
		I.	II.	III.	IV.
C	72.18	71.50	71.81	71.80	...
H	5.26	5.62	5.70	5.53	...
N	10.52	...	...	...	10.44
O	12.03	...	...	...	...
	99.99				

Bromine addition product of fumaric dianilide, $C_2H_2Br_2(CONHC_6H_5)_2$.—The fumaric dianilide unites with two atoms of bromine, and is thereby in all probability changed into the anilide of ordinary dibromsuccinic acid. If a solution of fumaric dianilide in glacial acetic acid be treated with the theoretical amount of bromine and heated to 100° in a closed tube till the color of the bromine has disappeared, the addition product is obtained as a white powder, which does not melt even at 100°.

0.1943 gram substance gave 0.1708 gram AgBr.

	Theory for $C_{16}H_{14}Br_2O_2N_2$.	Found.
Br	37.55	37.41

We shall attempt to prepare the anilide of ordinary dibromsuccinic acid directly from its chloride, in order to compare it with the bromine addition product of fumaric dianilide.

The substance, which Michael and Wing recently stated to be fumaric dianilide, is entirely different from the fumaric dianilide obtained by us from fumaryl chloride and aniline. The above-named chemists observed, during the gradual heating of monoaniline malate to 230°-250°, the formation of a yellow substance crystallising in needles which, after several recrystallisations from water, melted at 87.5°. Its analysis gave figures agreeing with the formula for fumaric dianilide. The results of the analyses, together with the fact that this compound was totally different from one of like composition which melts at 211°, and which is formed from maleic acid and aniline, very likely led Michael and Wing to the assertion that the compound melting at 87.5° was apparently fumaric dianilide.

Owing to these unintelligible contradictions we have repeated the distillation of monoaniline malate.

Monoaniline malate, $COOH.CH_2.CHOH.COOH.NH_2C_6H_5$.—The aniline salt of malic acid is, like the ammonium salt, easy to prepare in a crystalline condition. The assumption that the aniline unites with that carboxyl which is in combination with the CHOH group, and not with the other carboxyl, appears to be justified. The monoaniline malate is conveniently prepared by treating an alcoholic solution of malic acid with aniline. The employment of 21 grams aniline and 30 grams malic acid gave 47 grams of the salt after the first crystallisation, while the theoretical yield is only 51 grams. The monoaniline malate consists of small white prisms melting at 143°-144°.

I. 0.1793 gram substance gave 0.3481 gram CO_2 and 0.1014 gram H_2O.

II. 0.1673 gram substance gave 0.3240 gram CO_2 and 0.0905 gram H_2O.

III. 0.1619 gram substance gave 0.3127 gram CO_2 and 0.0893 gram H_2O.

	Theory for		Found.		
	$C_{16}H_{20}N_2O_5$.	$C_{10}H_{13}NO_5$.	I.	II.	III.
C	58.18	52.85	52.95	52.82	52.67
H	6.06	5.74	6.28	6.01	6.13
N	8.48	6.18	...	...	...
O	27.27	35.23	...	...	...

Distillation of monoaniline malate.—On subjecting monoaniline malate to distillation under ordinary pressure, the operation being conducted in a small retort placed in a graphite bath, water and aniline first go over, then yellow needles sublime, and later the portion which distills solidifies to a yellowish-white mass. A black viscous substance finally remains in the retort. The monoaniline malate gives a greater yield of the distillate by being first heated to 230°, then subjected to distillation under diminished pressure. 50 grams monoaniline malate gave 31 grams solid distillate. On treatment of the distillate with alcohol, the yellow substance goes into solution, while by far the greater part of the solid mass remains as a brown powder. That portion which was difficultly soluble in alcohol proved to be the so-called *maleic dianilide*, with the melting point 211°. After one recrystallisation from glacial acetic acid it gave the following figures:

I. 0.1729 gram substance gave 0.4543 gram CO_2 and 0.0894 gram H_2O.

II. 0.3870 gram substance gave 36.5 cc. N at 9.7° under 761.5 mm. pressure.

	Theory for $C_{16}H_{14}O_2N_2$.	Found. I.	Found. II.
C	72.18	71.66	...
H	5.26	5.74	...
O	12.03	...	...
N	10.52	...	11.35

The solid substance remaining after extraction with alcohol contained, besides a little maleic dianilide, the yellow-colored compound, which was extracted with benzene and precipitated with naphtha. After being several times dissolved in benzene and precipitated with naphtha it was obtained in a pure condition. The results of its analysis as well as its behavior prove this substance to be *maleinanil*.

Maleinanil, $C_2H_2(CO)_2N.C_6H_5$, melts, after several recrystallisations from low-boiling naphtha to which a little benzene is added, at 90°–91°, and consists of long yellow needles. It is easily soluble in benzene, chloroform, ether, and alcohol, difficultly soluble in carbon disulphide and low-boiling naphtha. On gradually cooling a solution of maleinanil in hot water, in which it is difficultly soluble, long yellow and often curved needles separate. The manner in which maleinanil crystallises from water reminds one of citraconanil.

One of us (A.), conjointly with W. O. Emery, determined the boiling point of maleinanil and of citraconanil under greatly diminished pressure.

Maleinanil boils at 162.1°–162.3° under 12 mm. pressure (temperature of paraffin bath 179°).

Citraconanil boils at 171.7° under 12 mm. pressure (temperature of paraffin bath 190°).

I. 0.2005 gram substance burned with lead chromate gave 0.5120 gram CO_2 and 0.0831 gram H_2O.

II. 0.1795 gram substance gave 0.4555 gram CO_2 and 0.0729 gram H_2O.

III. 0.3625 gram substance gave 25.8 cc. N at 10.5° and 767 mm.

IV. 0.3694 gram substance gave 24.3 cc. N at 4.7° and 759 mm.

	Theory for $C_{10}H_7O_2N$.	Found.			
		I.	II.	III.	IV.
C	69.37	69.64	69.21	...	...
H	4.04	4.60	4.51	...	...
O	18.49	...	...	...	...
N	8.09	...	...	8.58	8.04

In order to show the direct relation of maleinanil to maleic acid we treated maleic anhydride with aniline, in the proportion of equal molecules, and distilled the resulting product. Under these conditions the so-called maleic dianilide was the chief product, and it was accompanied by maleinanil, which could easily be detected by the method already mentioned.

Either the maleinanil or the so-called maleic dianilide is the principal product, according to the manner of conducting the distillation of monoaniline malate. The above-cited distillation of 50 grams monoaniline malate gave 31 grams distillate, from which were obtained 18 grams of the so-called dianilide and 7 grams of anil. If, on the other hand, the distillation be conducted under a pressure of 12 mm. and in a paraffin bath heated to 215°, much larger quantities of anil are formed, while the so-called maleic dianilide occurs in relatively smaller quantities. The formation of the latter substance in this decomposition was overlooked by Michael and Wing. The contradiction between their statements and our own, in relation to the properties of fumaric dianilide, has found an explanation in a surprising way. What Michael and Wing believed to be fumaric dianilide is nothing but maleinanil. That our preparation shows the melting point 90°–91°,

instead of 87.5°, perhaps indicates its greater degree of purity. How the different analytical results of Michael and Wing are to be explained we cannot conjecture, since the figures given by the above-named chemists are doubtless distorted through typographical errors. Not only is the percentage of N in $C_{16}H_{14}N_2O_2$ incorrectly stated, but also the percentage of N is incorrectly calculated from the data. We write the figures calculated by us from Michael and Wing's statements in brackets beside those taken from their paper.[1]

"0.2872 gram substance gave 0.7642 gram CO_2 and 0.1262 gram H_2O.

0.1484 gram substance gave 18 cc. N at 21° and 750 mm.

	Theory for $C_2H_2(CONHC_6H_5)_2$.	Found.
C	72.10 (72.18)	72.55 (72.57)
H	5.26 (5.26)	4.86 (4.88)
N	9.82 (10.52)	10.19 (13.63)".

The complete explanation of the constitution of maleinanil, which has one of the following formulas,

I. $\begin{matrix} CH.CN.C_6H_5 \\ \| \quad >O \\ CH.CO \end{matrix}$; II. $\begin{matrix} CH.CO \\ \| \quad >N.C_6H_5, \\ CH.CO \end{matrix}$

will require further experiments.

Dibromsuccinanil, $C_4H_3Br_2O_2NC_6H_5$, is easily prepared by treating a solution of maleinanil in chloroform with bromine. It gives, after recrystallisation from chloroform, white crystalline crusts, melting at 158°–159°.

0.2663 gram substance, heated in a closed tube with concentrated nitric acid, gave 0.3051 gram AgBr.

	Theory for $C_{10}H_7O_2Br_2N$.	Found.
Br	48.05	48.75

Fumaranilic acid, $\begin{matrix} CH.CONC_6H_5 \\ \| \\ CH.COOH \end{matrix}$.—By this name we indicate the anilic acid obtained by careful treatment of maleinanil with alkalies, since by the energetic action of alkalies it is converted into fumaric acid.[2]

[1] See note by Michael, this Journal **9**, 184.—Ed.

[2] This astonishing fact forms at first sight one of the arguments by means of which I seek in the following paper, "On the Isomerism of Fumaric and Maleic Acids," to establish my opinion regarding this kind of isomerism, and it will therefore be further discussed in the proper place.

Maleinanil, like citraconanil, dissolves readily in ammonia by gentle warming. By means of hydrochloric acid a precipitate is obtained from this solution which, after being several times dissolved and precipitated, gave the melting point 183°–184°. As the analysis of this product always gave too high a percentage of carbon, we substituted for ammonia barium hydrate solution, according to the method of Menschutkin.[1]

In this reaction too high a temperature must not be used, nor must the heating be continued too long, lest the decomposition go too far, in which case great loss of fumaranilic acid would result. In order to retain the carbonic acid the maleinanil is warmed to 30°–40° in a closed tube with a slight excess of a solution of barium hydrate, its solution being aided by frequent and violent shaking. If the mixture be heated for a time at 100°, considerable quantities of monobarium fumarate separate. The solution of the barium salt is next saturated with carbon dioxide to free it from excess of barium hydroxide, the barium carbonate separated by filtration, after which the fumaranilic acid is precipitated in the cold with hydrochloric acid. After several recrystallisations from alcohol the fumaranilic acid is obtained in prisms of a faint yellow color. These melt at 187°–187.5°, and are difficultly soluble in water.

I. 0.1689 gram substance burned with lead chromate gave 0.3873 gram CO_2 and 0.0734 gram H_2O.

II. 0.1360 gram substance gave 0.3122 gram CO_2 and 0.0592 gram H_2O.

III. 0.3954 gram substance gave 24.6 cc. N at 4.5° and 762 mm.

	Theory for $C_{10}H_9NO_3$.	Found.		
		I.	II.	III.
C	62.82	62.54	62.60	...
H	4.71	4.82	4.83	...
N	7.33	...	...	7.64
O	25.13	...	...	...

Upon heating the fumaranilic acid with a slight excess of a concentrated solution of alcoholic potash in a closed tube, potassium fumarate separates after a short time. After filtration the salt is dissolved in water, then acidified with hydrochloric acid, when pure fumaric acid is obtained. Although we were convinced that we had obtained fumaric acid by its conduct on heating, its

[1] Annalen der Chemie **162**, 176.

difficult solubility in water and the insolubility of its barium salt, we nevertheless analysed the free acid.

0.1752 gram substance gave 0.2667 gram CO_2 and 0.0592 gram H_2O.

	Theory for $C_4H_4O_4$.	Found.
C	41.38	41.51
H	3.45	3.74
O	55.17	...

After these results it was especially interesting for us to compare the maleinanilic acid with the fumaranilic acid obtained from maleinanil. Michael and Palmer make only a brief statement concerning the maleinanilic acid, which, however, does not at all agree with our own experience. According to Michael and Palmer the maleinanilic acid is formed in the following manner: "If a solution of one part maleic acid in ten parts of water be treated with enough aniline to form the acid salt, and if this solution be allowed to stand for a few days, the gradual separation of a crystalline substance is observed, which, after recrystallisation from alcohol, consists of prisms melting at 207°. This compound has the constitution $C_2H_2\begin{cases}CO.NHC_6H_5\\COOH\end{cases}$. It is readily soluble in alkalies, but insoluble in hydrochloric acid." This reaction has already been studied by W. H. Perkin,[1] who first investigated the behavior of fumaric and maleic acids towards aniline, and has made the following communication: "If a solution of aniline maleate be evaporated to dryness and the residue be allowed to stand for some time, it becomes entirely insoluble in water, and gives a product which crystallises from alcohol in beautiful needles, melting at 210°–211°. This compound is probably analogous to citraconanil."

"If a saturated solution of aniline maleate be allowed to stand some time in the cold, a crystalline substance separates, which is, however, different from that just described, and is soluble in hot water."

The product, first mentioned by Perkin, is doubtless identical with that which we obtained, together with maleinanil, by distilling monoaniline malate, and is also identical with the compound which Michael believed to be maleic dianilide. We shall show later that both these views are incorrect, and that the substance in question must be regarded as the anil of phenylaspartic acid.

[1] Berichte der deutschen chemischen Gesellschaft **14**, 2547.

But first we will turn our attention to a description of our experience in investigating the spontaneous decomposition of aniline maleate in a water solution. Our researches in this direction are, however, not yet completed.

Change of Aniline Maleate in Water Solution.

Monoaniline maleate, obtained by mixing a warm concentrated solution of maleic acid with the theoretical amount of aniline, crystallises in large transparent prisms, which, according to the analyses, contain half a molecule of water of crystallisation.

I. 0.2525 gram substance burned with lead chromate gave 0.5066 CO_2 and 0.1206 gram H_2O.

II. 0.2474 gram substance gave 0.4955 gram CO_2 and 0.1235 gram H_2O.

	Theory for		Found.	
	$C_{10}H_{11}O_4N$.	$C_{10}H_{11}O_4N + \frac{1}{2}H_2O$.	I.	II.
C	57.41	55.05	54.71	54.62
H	5.26	5.51	5.30	5.54
O	30.62	33.02	...	...
N	6.70	6.42	...	...

On dissolving the pure and readily soluble salt in a small quantity of water at the ordinary temperature, and allowing the solution to stand, a yellowish-white or often light brown crystalline mass separates, which, though amorphous, is apparently homogeneous. It became evident, however, in an attempt to determine the melting point, that we had a mixture, since the substance began to soften at 130°, melted partially on further heating, without, however, becoming completely liquid at 210°. We find ourselves in contradiction with Michael and Palmer as regards the melting point, and also as regards their statement that the transformation product is insoluble in alkalies and acids.

We have studied the gradual formation of this difficultly soluble substance by means of the balance, and we give some of our observations.

36 grams monoaniline maleate dissolved in somewhat more than 50 cc. H_2O gave:

1. Portion after 24 hours, 0.6 gram.
2. " " 24 " 0.67 "
3. " " 24 " 0.91 "
4. " " 24 " 0.50 "

5. Portion after 48 hours, 2.00 gram.
6. " " 48 " 3.00 "
7. " " 48 " 3.00 " etc.

At first there were found, together with the amorphous products of transformation, crystals of unchanged monoaniline maleate, which, before filtration, were dissolved by gently warming the solution. The separated mass was often more or less brown in color. A series of combustions of the washed and dried substance was made, the results of two of which we give, as the substance here employed was remarkably pure and homogeneous.

I. 0.2004 gram substance burned with lead chromate gave 0.4146 gram CO_2 and 0.0987 gram H_2O.

II. 0.2147 gram substance gave 0.4480 gram CO_2 and 0.1063 gram H_2O.

	Theory for $C_{16}H_9NO_3$.	Theory for $C_{10}H_{11}NO_4$.	Found. I.	Found. II.
C	62.82	57.41	56.42	56.91
H	4.71	5.26	5.47	5.50

The percentages found are quite different from those required by maleinanil; they, however, approach those values required by maleinanil plus one molecule of water; that is, for monoaniline maleate.

In any case, there occur among the transformation products of monoaniline maleate small quantities of phenylaspartic acid, and a derivative of phenylaspartic acid, which will farther on be discussed at length. This led us to think that perhaps the aniline salt of inactive malic acid was formed as an intermediate product. The main part of the transformation product, however, is quite closely related to maleic acid. On treatment with barium hydrate there is formed, together with other barium salts, which have not yet been investigated, a barium salt crystallising in silver-white leaflets, the analyses of which gave figures agreeing with anhydrous barium malate. The crystals were, however, nothing but the barium salt of maleic acid + $1H_2O$.

I. 0.3824 gram substance burned with lead chromate gave 0.2436 gram CO_2 and 0.0561 gram H_2O.

II. 0.1139 gram substance gave 0.0987 gram $BaSO_4$.

III. 0.2265 gram substance gave 0.1958 gram $BaSO_4$.

IV. 0.1544 gram substance gave 0.1330 gram $BaSO_4$.

V. 1.7267 grams substance lost at 100° in a Liebig's drying tube 0.1199 gram H_2O.

	Theory for $C_4H_3O_4Ba + 1$ Aq.	Found. I.	II.	III.	IV.	V.
C	17.84	17.37	...	...	...	...
H	1.49	1.63	...	...	...	...
O	29.74	...	...	...	...	...
Ba	50.93	...	50.95	50.82	50.65	...
	100.00					
Aq	6.69	...	...	...	...	6.94

On treatment of the barium salt with sulphuric acid in the proportion of the molecular weights, we obtained without difficulty pure maleic acid, melting at 130°–131°.

Unfortunately we have not as yet been able to separate, by crystallisation, the transformation products of monoaniline maleate. We must therefore reserve for later research the determination of the relation in which the chief product stands to maleic acid.

On treating the last mother-liquors from the barium salts of the transformation products of monoaniline maleate with hydrochloric acid we obtained after a time a small quantity of well-formed crystals. The same crystals are formed when the transformation product is dissolved directly in hydrochloric acid. They appear to be formed in larger quantities when the solution of monoaniline maleate is allowed to stand a long time by itself. We have not as yet investigated their properties. The base of the hydrochloric acid salt is readily soluble in alkalies and alkaline earths. After a consideration of these peculiarities one is led to suspect the presence of an amido acid. Indeed, the analyses of the hydrochloric acid salt as well as those of the free acid; further, the synthesis of the latter from monobromsuccinic acid and aniline, all indicate the presence of phenylaspartic acid. The hydrochloric acid salt crystallised from water gave analyses agreeing with the following formula for phenylaspartic acid hydrochloride:

$$C_{20}H_{27}N_3O_{10}Cl = [C_2H_3NHC_6H_5.(COOH)_2]_2 + HCl + 2H_2O.$$

I. 0.2008 gram substance gave 0.3577 gram CO_2 and 0.1043 gram H_2O.

II. 0.2105 gram substance gave 0.3764 gram CO_2 and 0.1080 gram H_2O.

III. 0.2155 gram substance gave 0.0640 gram AgCl.

	Theory for $C_{20}H_{27}N_3O_{10}Cl$.	Found. I.	II.	III.
C	48.91	48.58	48.76	...
H	5.50	5.77	5.70	...
N	5.70	...	...	...
O	32.62	...	...	...
Cl	7.24	...	...	7.34
	99.97			

As is well known, the amido fatty acids—for example, amido acetic acid—have the property of forming salts with hydrochloric acid, in which two molecules of the amido acid and one molecule of hydrochloric acid occur; the formula, then, for the hydrochloride of phenylaspartic acid is not surprising.

Synthesis of Phenylaspartic Acid.

As to prove by means of a breaking down of the substance that it is phenylaspartic acid might be a difficult matter, we attempted to make phenylaspartic acid synthetically from monobromsuccinic acid and aniline.

The monobromsuccinic acid was prepared by treating fumaric acid with a saturated solution of hydrobromic acid in glacial acetic acid.[1] A concentrated water solution of the acid thus obtained was boiled a short time with aniline. On cooling, the phenylaspartic acid gradually separated from the solution. The acid so obtained is by no means pure. Some of the impurities remain behind on treating the crude phenylaspartic acid with hydrochloric acid. The hydrochloride of phenylaspartic acid then separates from the acid filtrate in well-formed crystals, which, after recrystallisation from water, are pure.

I. 0.2092 gram substance burned with lead chromate gave 0.3682 gram CO_2 and 0.1057 gram H_2O.

II. 0.2033 gram substance gave 0.3635 gram CO_2 and 0.1061 gram H_2O.

III. 0.2600 gram substance gave 0.0788 gram AgCl.

IV. 0.1664 gram substance gave 0.0485 gram AgCl.

V. 0.2128 gram substance gave 0.0626 gram AgCl.

[1] Berichte der deutschen chemischen Gesellschaft **11**, 1221.

	Theory for $C_{20}H_{27}N_2O_{10}Cl$.	Found. I.	II.	III.	IV.	V.
C	48.91	48.00	48.76	...	...	...
H	5.50	5.60	5.79	...	...	...
N	5.70	...	...	...	...	...
O	32.62	...	...	...	...	...
Cl	7.24	...	...	7.49	7.21	7.27
	99.97					

The hydrochloride of phenylaspartic acid from monobromsuccinic acid and aniline has therefore the same composition as the phenylaspartic acid hydrochloride obtained from monoaniline maleate. The proof of the identity of both phenylaspartic acid hydrochlorides from different sources is most effectually furnished by the crystallographic evidence, for which we are indebted to Professor Dr. Hintze, who has made a study of the crystals in the Institute of the University of Breslau. He says:

"The monosymmetrical crystals are combinations of prism p (110) ∞P and base c (001) oP, the acute prism-angle being bisected by the plane of symmetry. Although the crystals are bright, still the planes are curved and broken, therefore unsuited for exact measurements. Still, there can be no doubt as to the identity of the several crystallisations of the compound, the one α from monobromsuccinic acid and aniline, the other β from monoaniline maleate. The measurements made by G. Laird in the Mineralogical Institute of Breslau gave different results for different crystals:

	α.	β.	
for $p:p = 110:1\bar{1}0$,	53°30′–55°	54°–55°30′	Plane angle.
for $p:c = 110:001$,	96°30′–97°30′	96°–97°20′	Plane angle.

"An average of the best measurements:

$$p:p = 110:1\bar{1}0 = 54°50'$$
$$p:c = 110:001 = 96°50'$$

gives the ratio of the axes:

$$a:b = 1.9957:1$$
$$\beta = 75°\ 1.5'.$$

"The base is often inclined to a positive hemidoma. Distinct cleavage in the direction (100) $\infty\breve{P}\infty$. The direction of extinction on the planes of the prism forms with the vertical edge of the prism an angle of about 35°."

Phenylaspartic acid, $C_6H_5NH.C_6H_5(COOH)_2$.—On treating a known weight of phenylaspartic acid hydrochloride with the theoretical quantity of moist silver hydrate, filtering from the silver chloride and evaporating the filtrate in a vacuum desiccator, white masses of phenylaspartic acid gradually separate from the solution. If a solution of phenylaspartic acid be allowed to crystallise slowly, small crystals are formed, which we hope to obtain later in a form suitable for crystallographic measurements.

I. 0.1139 gram substance burned with chromate of lead gave 0.2401 gram CO_2 and 0.0564 gram H_2O.

II. 0.2282 gram substance gave 0.4815 gram CO_2 and 0.1093 gram H_2O.

III. 0.4185 gram substance gave 23.2 cc. N at 4.5° and 772 mm.

		Found.		
	Theory for $C_{10}H_{11}O_4N$.	I.	II.	III.
C	57.41	57.49	57.54	...
H	5.26	5.50	5.32	...
N	6.70	...	...	6.90
O	30.62	...	...	...
	99.99			

The pure phenylaspartic acid melts without decomposition at 131°–132°; acquires, however, at 121° a doughy consistency.

Phenylaspartanil, $C_6H_5NH.C_6H_3.C_2O_2NC_6H_5$.—In describing the distillation of monoaniline malate we have already stated that, besides the maleinanil as the chief product, a substance was formed which is evidently identical with that obtained by Michael and called by him maleic dianilide. As has already been stated, this substance is also formed by heating maleic anhydride with aniline; at the same time a little maleinanil is formed. In closing the description of fumaric acid anil we took the opportunity of stating that W. H. Perkin had already, in 1881, made researches on the action of aniline upon fumaric and maleic acids, and had also observed the formation from maleic acid of a compound melting at 210°–211°. He regarded this compound as maleinanil, in the belief that it corresponded to citraconanil. At that time Perkin called attention to the fact that aniline fumarate and mesaconate gave no products insoluble in water on evaporating their solutions; while, on concentrating a solution of citraconate of

aniline, citraconanil was formed. Michael seems to have overlooked this statement of Perkin.[1]

After the foregoing, it is hardly necessary that special reference be made to the contradictions in the statements of W. H. Perkin and of Michael concerning the substance melting at 210°–211°.

We repeated the experiment of Michael, and obtained from 5 grams maleic acid, 0.9 gram of a crude product insoluble in water and melting at 195°–199°. After recrystallisation from alcohol the correct melting point, 211°, was observed.

I. 0.1864 gram substance burned with lead chromate gave 0.4920 gram CO_2 and 0.0870 gram H_2O.

II. 0.1635 gram substance gave 0.4326 gram CO_2 and 0.0801 gram H_2O.

	Theory for $C_{16}H_{14}N_2O_2$.	Found. I.	II.
C	72.18	71.97	72.16
H	5.26	5.18	5.44
N	10.52	...	...
O	12.03	...	...
	99.99		

The analyses prove that the compound obtained from maleic acid and aniline is not maleinanil, but is isomeric with fumaric dianilide described above. The nature of the substance was shown by its decomposition at 100° in a closed tube with alcoholic potash.

Instead of the potassium salt of maleic acid, the formation of which would naturally be expected from maleic dianilide, the potassium salt of phenylaspartic acid was obtained, which, on treatment with hydrochloric acid, gave phenylaspartic acid hydrochloride. The splitting off of the aniline residue is more easily effected if the substance be heated at 100° with fuming hydrochloric acid instead of potassium hydrate. After concentration in a vacuum the phenylaspartic acid hydrochloride crystallises out.

I. 0.1984 gram substance gave 0.3563 gram CO_2 and 0.1033 gram H_2O.

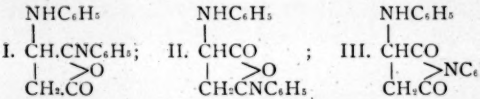
II. 0.2317 gram substance gave 0.0636 gram AgCl.

III. 0.1625 gram substance gave 0.0448 gram AgCl.

[1] See note by Michael, this Journal **9**, 183.—Ed.

	Theory for $C_{20}H_{27}O_{10}N_2Cl$.	Found. I.	II.	III.
C	48.93	48.97	...	...
H	5.50	5.78	...	...
O	32.62	...	...	...
N	5.71	...	...	...
Cl	7.24	...	6.80	6.84
	100.00			

The substance melting at 210°–211° is therefore to be regarded as phenylaspartanil, and must be represented by one of the three following formulas:



but which of the three is the correct one we are as yet not in a position to decide.

The easily prepared phenylaspartanil forms the most convenient material from which to prepare phenylaspartic acid; moreover, this acid, together with its dianilide, was obtained by Piutti[1] by heating powdered asparagine with dry aniline. He gives as the melting point of phenylaspartanil 209°. From this anil the phenylaspartic acid was obtained; but Piutti did not carry his researches farther than its formation. The formation of phenylaspartic acid from maleic acid and aniline may be explained in different ways.

The question is, Does the aniline unite directly with the maleic acid, or is the maleic acid, by union with water in the presence of aniline, first converted into monoaniline malate, from which, by the splitting off of water, phenylaspartic acid is formed; or have we in the formation of phenylaspartic acid an example similar to that of the transformation of unsaturated acids into γ-lactones; for example, that of pyroterebic acid into isocaprolactone?

The formation of phenylaspartic acid from maleic acid and aniline speaks in favor of the above-mentioned possibilities. On heating equal molecular weights of maleinanil and aniline for a time in a closed tube at 100°, the yellow solution is gradually changed

[1] Gazz. chim. ital. **14**, 474, Anm.

into a solid white substance having all the peculiarities of phenylaspartanil prepared in other ways.

Whether the formation of phenylaspartanil by boiling a solution of monoaniline maleate, or by heating maleic anhydride with aniline, or, further, from monoaniline malate, takes place after the formation, first of maleinanil, then of phenylaspartic acid, or *vice versa*, we are not as yet in a position to decide.

The formation of phenylaspartanil is, in a certain sense, analogous to the formation of aldehyde ammonia, in which case the ammonia breaks the double bond existing between carbon and oxygen, and unites with the aldehyde; exactly in the same way the addition of maleinanil results after the double bond between the carbon atoms has been broken.

To the best of our knowledge, this breaking of the double bond between carbon atoms by aniline is the first example of such a reaction, the generalisation of which we wish to reserve for further research.

The results of the investigation are, briefly: From fumaryl chloride and aniline, fumaric dianilide is formed, which, on treatment with an alcoholic solution of potassium hydrate, gives fumaric acid. The supposed dianilide of maleic acid has been proved to be phenylaspartanil.

We obtained phenylaspartic acid:

1. From monoaniline maleate.
2. From its anil.
3. From monobromsuccinic acid and aniline.

The anil of phenylaspartic acid is formed:

1. From aniline maleate (boiling of its water solution).
2. By heating:
   - *a.* Maleic acid and aniline.
   - *b.* Maleic anhydride and aniline.
   - *c.* Monoaniline malate.
   - *d.* Maleinanil and aniline.

In both the reactions 2 *b* and 2 *c* there is formed, besides phenylaspartanil, maleinanil, which has been regarded as fumaric dianilide. We converted maleinanil into fumaranilic acid, and this in turn into fumaric acid.

Whether the maleinanil is the chief transformation product when a water solution of monoaniline maleate is allowed to stand for a time must be decided by further investigations.

It follows from the foregoing comparison that the study of the anilides of fumaric and maleic acids is, in many directions, incomplete. Researches originally planned have not yet been undertaken; new problems present themselves, owing to the unexpected results of some of the reactions. In consideration of these results, the anils and anilides of all the dicarbon acids standing in theoretical relation to fumaric and maleic acids require a new investigation, as a check to that already carried out. The change undergone by monoaniline maleate in water solution needs, first of all, a careful research, which will necessarily occupy us for some time.

We propose to include in the circle of our investigations the amides and imides of fumaric, maleic, and malic acids. For, without doubt, the question concerning the constitution of the so-called fumarimide stands in the closest relation to these problems. This compound is formed by heating ammonium malate, and is readily convertible into inactive aspartic acid.[1]

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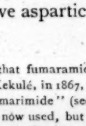
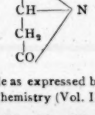
[1] The assertion of Michael and Wing that fumaramide is not a fumaric acid derivative is certainly correct, but not entirely new. Kekulé, in 1867, in Vol. II of his Lehrbuch, invariably speaks of fumarimide as the "so-called fumarimide" (see pp. 179-81). At that time structural formulas were not employed in the sense now used, but "typical formulas," which can, however, as Ladenburg has already done (compare Vortraege ueber die Entwickelungsgeschichte der Chemie, 2d edition, p. 278), be converted into modern structural formulas by the aid of the so-called "graphical formulas" to be found in Kekulé's Lehrbuch. From the observations of Kekulé, it is quite evident that he regarded the alcoholic hydroxyl group as participating in the formation of fumarimide, and if the formula given by him for the so-called fumarimide be translated into the language of our modern formulas, the following structural formula is obtained:



The structural formula of fumarimide as expressed by Michael and Wing is introduced in Roscoe and Schorlemmer's Manual of Chemistry (Vol. III, p. 812, 1884) as follows:



This formula is also intended to represent the change of the so-called fumarimide into aspartic acid. But the constitution of fumarimide is still entirely doubtful, and it is therefore difficult to understand why Michael and Wing desire to abandon the name fumarimide before we really know what kind of a substance is to be understood by this name.—R. ANSCHÜTZ.

CONCERNING THE ISOMERISM OF FUMARIC AND MALEIC ACIDS.[1]

By Richard Anschütz.

That kind of isomerism which is observed between fumaric and maleic acids is gradually acquiring more significance since a large number of organic compounds have begun to be classed in the same category, partly with and partly without grounds for such classification. The apparent simplicity of the composition of fumaric and maleic acids, their close relationship to many organic compounds of known constitution, the remarkable changes of both acids and some of their derivatives into one another, the intimate relation to the isomeric malic acids, to the tartaric acids and to the compounds of the furfuran group, make the discovery of a satisfactory explanation, supported by experiments, of the isomerism of fumaric and maleic acids a problem, the solution of which promises to be of fundamental importance to organic chemistry. Before I present my views on this subject it will not be out of place to summarise the most important hypotheses already proposed having for their object the explanation of the isomerism of fumaric and maleic acids, and, secondly, to discuss these hypotheses.

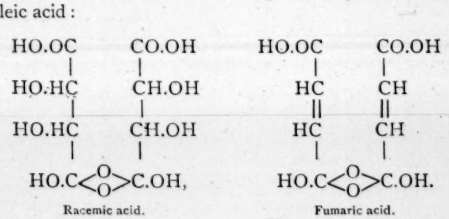
These can be divided into two classes: 1. Those in which it is assumed that the molecule of one acid is twice as large as that of the other; 2. Those in which it is assumed that both have the same molecular weight.

As early as 1838 Liebig[2] in the first of his classical memoirs "On the Constitution of Organic Acids" expressed himself as follows concerning the relation between fumaric and maleic acids: "It is possible that equisitic acid [the name then used for maleic acid] is $C_8H_4O_6 + 2Aq$, and fumaric acid $C_4H_2O_3 + Aq$, that is, that the transformation of one into the other takes place in a manner similar to that of cyanic into cyanuric acid, in which, as is well known, a molecule of the one splits up into three of the other." This conception harmonises with that of Erlenmeyer,[3] who in 1870 made the following communication on the possible formation of polymeric modifications of carbonic acids: "I consider it possible, and indeed probable, that in the case of acids as well as of

[1] Communicated by the author. [2] Annalen der Chemie **26**, 168.
[3] Berichte d. deutsch. chem. Gesell. **3**, 243.

aldehydes—the acids being in fact nothing but hydroxy-aldehydes —polymeric compounds occur, so that two or more molecules of different acids can unite to form a larger chemical molecule. This assumption would help to explain not only margaric acid, cinnamic acid (elaidic acid?), but also racemic acid, and perhaps maleic acid, as well as many peculiar relations observed in the conduct of certain other acids."

On account of the great analogy which the exhaustive researches of Kekulé[1] and of Fittig[2] have shown to exist between mesaconic and fumaric acids, on the one hand, and citraconic and maleic acids on the other, it would appear to be justifiable to apply to the analogous acid an hypothesis put forward to explain one of these acids. I mention this because Henry[3] in 1875 regarded mesaconic acid as being in all probability a polymeric modification of citraconic acid. One year later Markownikoff[4] was of the decided opinion that mesaconic acid is a polymeric modification of citraconic acid. This belief on the part of Markownikoff as well as of Henry was occasioned by a consideration of the melting points of the two acids, and of the fact that citraconic acid is changed to mesaconic acid by heating it with nitric, hydrochloric, or hydriodic acid. In harmony with this view of Markownikoff is the view of Erlenmeyer[5] recently communicated. Contrary to his former belief, he regards fumaric acid as a polymer of maleic acid, having a constitution similar to that of racemic acid. He says: "Racemic acid is certainly a double molecule, composed of dextro and lævo-tartaric acids; fumaric acid is as certainly made up of two molecules of maleic acid:



Racemic acid. Fumaric acid.

This conception has indeed much to commend it. It was

[1] Annalen der Chemie, Sup. **1**, 129, 338; **2**, 85.
[2] Ibid. **188**, 42; **195**, 56, 169.
[3] Bull. Soc. Chim. **23**, 353.
[4] Annalen der Chemie **182**, 356.
[5] Berichte d. deutsch. chem. Gesell. **19**, 1937.

shown some years ago by Kekulé and myself[1] that a generic relation exists between racemic and fumaric acids on the one hand and inactive tartaric and maleic acids on the other, since by oxidation with potassium permanganate, fumaric and maleic acids are converted into racemic and inactive tartaric acids respectively. At the close of our second paper we drew from these facts the following conclusion: "The nature of the isomerism of fumaric and maleic acids may perhaps be the same as that between racemic and inactive tartaric acids. Then, besides the inactive, there ought to exist two active modifications of maleic acid which should be obtained by the breaking up of fumaric acid." I will mention here that numerous attempts have been made to split up fumaric acid into its optically active components, according to methods employed in other cases, but without success.

Although it would not perhaps be difficult to assume from the result of the oxidation that fumaric acid is made up of dextro and lævo-maleic acids, still it would not necessarily follow; in fact, such an assumption would be unjustifiable if the theory of van t'Hoff-Le Bel is correct.[2] According to this theory, formulas for fumaric and maleic acids have been deduced, according to which the acids differ only in the relative positions in space of the carboxyls to the CH groups. Accepting this suggestion, an experimental solution of the question with regard to the isomerism of fumaric and maleic acids would scarcely be possible. As it is, it cannot but seem remarkable that so slight a difference in the position of the carboxyl groups should be the cause of such a fundamental difference in properties as is actually shown by fumaric and maleic acids.

To repeat—the generic relation of fumaric and racemic acids which Kekulé and myself have shown to exist, forms at present the only foundation for the supposition that fumaric acid has twice as large a molecule as maleic acid.

Erlenmeyer's formulas for fumaric and maleic acids show a possibility "of explaining apparently abnormal cases of isomerism and other cases of apparently abnormal behavior of organic acids,"

[1] Berichte d. deutsch. chem. Gesell. **13**, 2150; **14**, 713; cf. Tanatar, ibid. **12**, 2293; **13**, 159, 1383; Kekulé, Annalen der Chemie **117**, 124; Annalen der Chemie, Supp. **1**, 375; Perkin and Duppa, ibid. **117**, 130; Pasteur, Annalen der Chemie, Supp. **2**, 242; Jungfleisch, Bull. Soc. chimique **19**, 50, 194; **41**, 214, 226; Wyrouboff, ibid. **41**, 210; Pasteur, ibid. **41**, 215; Anschütz, Annalen der Chemie **226**, 191.

[2] Le Bel, Bull. Soc. chimique **22**, 337; **37**, 300; van t'Hoff, Lagerung der Atome im Raume bearbeitet von F. Hermann: Braunschweig, 1877, pp. 13, 21, 29.

but no experimental evidence of the correctness of this view has as yet been furnished. The van t'Hoff-Le Bel theory, which is opposed to the assumption of the existence of a dextro and lævo-maleic acid, assumes the simplest formula for fumaric acid, CH.COOH
||
CH.COOH,
and ascribes the difference in properties of fumaric and maleic acids to different positions in space of the carboxyl groups.

I will now turn to the other hypotheses, according to which the fumaric and maleic acids have the same molecular weight, and the difference in the properties of the two acids is ascribed to a difference in the arrangement of the same number of atoms in the molecule. First, the chief argument in favor of the view that both acids have the same molecular weight will be considered as to its tenability.

It is often the custom, from the vapor density of a volatile derivative of a substance which is not itself volatile without decomposition, not only to draw conclusions concerning the molecular weight of the derivative, but also of the non-volatile substance itself in the solid state. Thus Hübner and Schreiber[1] have in this way shown that the vapor density of the ethyl ether of fumaric acid and that of maleic anhydride correspond to the simple formula of both substances. They have therefore concluded that the solid fumaric and maleic acids themselves must also possess an equal molecular weight corresponding to the simple formula $C_4H_4O_4$. It is evident that such a conclusion is wrong in principle, and, to demonstrate this, an ether of racemic acid appeared to me most suitable for showing the generic relation between racemic and fumaric acids. At my request a vapor density determination of the ethyl ether of racemic acid was made by my friend Bennert, according to Hofmann's method.[2] This determination was in accordance with the simple formula $C_8H_{14}O_6$. This result was not surprising, since the ethers of racemic and dextro-tartaric acids, with the same alcoholic radicals, possess the same boiling point under like conditions of pressure. I further prepared the methyl ether of lævo-tartaric acid, and proved that it united with equal parts by weight of the methyl ether of dextro-tartaric acid, forming the methyl ether of racemic acid. It must therefore be supposed that the ethers of

[1] Zeitschr. f. Chem. [N. F.] **7**, 712; cf. Hübner, Ber. d. deutsch. chem. Ges. **14**, 210.
[2] Anschütz, Ber. d. deutsch. chem. Ges. **18**, 1399.

racemic acid on being heated up to their boiling points, even under diminished pressure, are resolved into the ethers of dextro and lævo-tartaric acid, which, when their vapors are cooled, unite again to form the ethers of racemic acid. It is therefore certain, from the generic relation existing between racemic and fumaric acids, that the vapor density of the ether of fumaric acid leading to the simple formula $C_8H_{12}O_4$, is no satisfactory proof of the simple formula of this ether, nor of fumaric acid itself—that is, it is no argument against the assumption of a double molecule.[1]

It is generally conceded that the acid properties of fumaric and maleic acids are due to the presence of two carboxyl groups. The formulas which would first naturally suggest themselves are

Fumaric acid. Maleic acid.

or *vice versa*. This conception, formerly held by V. v. Richter[2] and others, has been generally abandoned, since it does not harmonise with the general behavior and the simplest changes of both acids. I need only mention the formation of one and the same ethylene-succinic acid from both acids, and the fact that neither fumaric nor maleic acid loses carbon dioxide when heated.

All this has been discussed so often that it appears to me superfluous to go over it again. Kekulé[3] has proposed, in order to explain the formation of ethylene-succinic acid by the reduction of both acids, that in one of them, the maleic acid, a carbon atom be assumed to have two free bonds. If the presence of bivalent carbon atoms in organic compounds be regarded as possible, then it cannot be denied that, as Fittig[4] has shown some ten years ago, a large number of reactions with fumaric and maleic acids can be very easily and elegantly explained by the aid of the "incomplete formula for maleic acid." The following formulas for fumaric and

[1] I will mention that I caused a series of vapor density determinations to be made in this laboratory, of the different ethers of fumaric and maleic acids, and of mesaconic and citraconic acids. All the results pointed to a simple formula. They will be published in full as soon as a fitting opportunity presents itself.

[2] Zeitschr. f. Chem. [N. F.] **4**, 453.

[3] Annalen der Chemie, Supp. **2**, 111; Zeitschrift für Chemie **6**, 12; cf. Kolbe, Zeitschrift für Chemie **6**, 13; Erlenmeyer, ibid. **6**, 21; Claus, Theoretische Betrachtungen und deren Anwendungen zur Systematik der organischen Chemie, 200: Freiburg i. B., 1867.

[4] Annalen der Chemie **188**, 100; Berichte d. deutsch. chem. Gesell. **10**, 518.

maleic acids are still considered by Fittig[1] to be the best constitutional expressions for both acids:

$$\begin{array}{l} CH.COOH \\ \| \\ CH.COOH, \end{array} \qquad \begin{array}{l} =C.COOH \\ | \\ CH_2.COOH. \end{array}$$

Fumaric acid. Maleic acid.

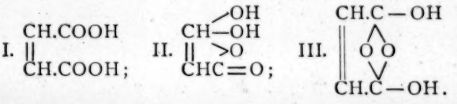
Beilstein[2] is of the same opinion, and so are most other chemists. If we ask ourselves why this formula be ascribed to maleic acid and not to fumaric, the answer may be found in the words of Rochleder,[3] who introduced the term "incomplete compound" into organic chemistry: "Maleic acid unites with bromine more readily than fumaric acid." Kekulé and Swarts,[4] at the close of their paper "On the Constitution of Itaconic, Citraconic, and Mesaconic Acids," express themselves as follows: "Fumaric acid is, for example, to be regarded as the analogue of mesaconic acid, and hence as the true homologue of mesaconic acid; in maleic acid, however, free bonds are assumed, and it is known in fact that maleic acid forms addition-compounds more readily than its isomer fumaric acid."

Without considering that the slow addition of bromine by fumaric acid is caused by its difficult solubility and that of its addition-product, the ethers of fumaric acid unite with bromine as readily as any compound of maleic acid.[5] Consequently, the strongest reason for giving preference to this formula, $\begin{array}{l} =C.COOH \\ | \\ CH_2COOH \end{array}$ for maleic acid does not exist, and I believe that my assertion made some years ago that, with the same right, the formula $\begin{array}{l} =C.COOH \\ | \\ CH_2.COOH \end{array}$ could be given to fumaric acid, and the formula $\begin{array}{l} CH.COOH \\ \| \\ CH.COOH \end{array}$ to maleic acid, was perfectly justifiable.

One of the principal objections to the free bond formula, whether it be given to fumaric or to maleic acid, is the formation of racemic acid and inactive tartaric acid from fumaric and from maleic acids.

[1] Lehrbuch der organischen Chemie, 1887. [2] Handbuch der organischen Chemie, 1886, **1**, 616.
[3] Zeitschrift für Chemie **7**, 261. [4] Zeitschrift für Chemie [N. F.] **3**, 651.
[5] Anschütz, Berichte d. deutsch. chem. Gesell. **12**, 2282; **10**, 1887.

These facts indicate that the group $\begin{matrix}CH\\ \|\\ CH\end{matrix}$ is present in both acids. The breaking up of the acids by electrolysis,[1] as well as the result obtained from the determination of the molecular refraction of their ethers,[2] lead to the same conclusion. If, however, the presence of the group $\begin{matrix}CH\\ \|\\ CH\end{matrix}$ be assumed in both acids, and it be assumed also that they have the same molecular weight, then the difference in their properties, if one does not seek refuge in van t'Hoff-Le Bel's hypothesis, must lie in the way the oxygen atoms and hydroxyl groups are united. In that case, of course, the view that in the molecule of each acid two carboxyls are contained must be abandoned. This leads to the three following conceivable formulas:



This possibility of escape from the dilemma with which organic chemistry is confronted by the isomerism of fumaric and maleic acids has hitherto received no attention, but it has already been mentioned twice, as far as I know, though only as a conjecture and without any effort to test it. As I shall now endeavor to *prove* that formula I. must be given fumaric acid, and that probably formula II. must be given to maleic acid, I will first quote certain statements of W. H. Perkin and W. Roser touching similar matters.

W. H. Perkin, Sen.,[3] found, among other things, that fumaric acid, on treatment with acetyl chloride, gives the same anhydride as maleic acid, and concerning this reaction he made the following observation:

"All these arguments apparently show the remarkable fact that only one anhydride is obtainable from fumaric and maleic acids, one only from citraconic and mesaconic acids, and, finally, only one from α and β-cumaric acids.

[1] Kekulé, Annalen der Chemie **131**, 87.

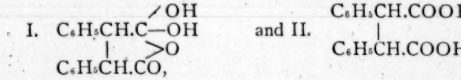
[2] Gladstone, Berichte d. deutsch. chem. Gesell. **14**, 2544; Brühl, ibid. **14**, 2736; Kannonikoff, Journal f. prak. Chemie [N. F.] **32**, 500. At my request C. Knops has determined the molecular refractions of 12 ethers of maleic, fumaric, citraconic, mesaconic, and itaconic acids. The results will soon be published.—Anschütz.

[3] Berichte d. deutsch. chem. Gesell. **14**, 2546.

"Upon what, then, can the isomerism of these acids depend, if not on the difference in position of the hydroxyl groups to the radicals?"

W. Roser expresses himself on this point much more decidedly:[1]

"The isomerism of the two diphenyldicarbonic acids, of the diphenylsuccinic acids, obtained by Reimer[2] from stilbene-dicarbonic acid, and which are converted into one another by treating either with hydrochloric acid or with barium hydrate, as the case may be, find a simple explanation in the following formulas:



"The corresponding relations of maleic and fumaric acids and of the cumaric acids can perhaps be most easily explained by means of similar formulas." Roser adds:

"If the ethers of phthalic acid be constituted analogously to the first formula—that is, $C_6H_4\begin{cases} C{=}(OC_2H_5)_2 \\ >O \\ CO, \end{cases}$ then their formation from phthalyl chloride is easily understood. On the other hand, there is indicated the possible existence of another isomeric phthalic acid and of another succinic acid."

It will be seen from the above how decidedly Roser's views have been influenced by the knowledge that the chloride of phthalic acid is unsymmetrically constituted. I will therefore call attention to the principal grounds for our present view regarding the constitution of this chloride.

As is well known, Hessert[3] first proved that by the reduction of phthalyl chloride there is formed, not the dialdehyde of *o*-phthalic acid, as was formerly supposed, but the inner anhydride of the *o*-alcohol-carbonic acid, $C_6H_4\begin{cases} CH_2OH\ (1) \\ COOH\ (2), \end{cases}$ to which he gave the name phthalide and the structural formula $C_6H_4{<}\begin{matrix} CH_2 \\ CO \end{matrix}{>}O$.

The counter-conclusion that phthalyl chloride is dichlorphthalide suggests itself, and is confirmed by the experiments of v. Baeyer,[4] who showed that phthalo-phenone, which is formed by treating

[1] Berichte d. deutsch. chem. Ges. **15**, 2347.
[2] Ibid. **14**, 1802.
[3] Ibid. **10**, 1445; **11**, 237.
[4] Annalen der Chemie **202**, 50.

phthalyl chloride and benzene with aluminic chloride, is a triphenylmethane derivative, viz. diphenylphthalide, $C_6H_4<\begin{matrix}C(C_6H_5)_2\\ \\ CO\end{matrix}>O$.

Proceeding on the supposition that phthalic acid contains two carboxyls and that therefore its silver salt should give symmetrical ethers, Graebe[1] attempted to obtain the unsymmetrical ethers from phthalyl chloride. In the case of phthalic acid itself he did not with certainty reach the expected result. With tetrachlorphthalic acid, however, he succeeded in preparing from the silver salt and ethyl iodide an ethyl ether melting at 60°, while from the chloride of tetrachlorphthalic acid and sodium alcoholate, the isomeric ethyl ether, melting at 124°, was obtained. Hence Graebe concludes: "There is here no other explanation possible than that the first compound has the formula $C_6H_4\begin{cases}CO_2C_2H_5\\ CO_2C_2H_5\end{cases}$; while the second has this formula, $C_6H_4\begin{cases}C(OC_2H_5)_2\\ >O\\ CO.\end{cases}$"

As the experimental proof for the existence of two tetrachlorphthalic acids was at that time wanting, Graebe did not consider the counter-conclusion based on the possibility of the existence of two isomeric tetrachlorphthalic acids. Again, the opinion that in a dicarbonic acid there must of necessity be two carboxyls was so deep-rooted that such formulas as $C_6Cl_4\begin{cases}\diagup OH\\ C-OH\\ >O\\ CO\end{cases}$ would not easily have been accepted without the most convincing proofs. Further, no difficulties were encountered in explaining the change of the chloride, $C_6H_4\begin{cases}CCl_2\\ >O\\ CO\end{cases}$, into the acid, as well as the reverse change.

The conception that many ketone-carbonic acids are oxylactones has recently been given an experimental basis by the important discovery of acetyl-lævulinic acid by Bredt.[2] Since the researches of Bredt, I no longer doubt that acetyl-lævulinic acid is to be regarded as γ-oxy-valero-lactone. I write the old and new formulas for the acid side by side:

[1] Berichte d. deutsch. chem. Gesell. **16**, 860. [2] Annalen der Chemie **236**, 225.

I. $\begin{matrix} CH_2.CO.CH_3 \\ | \\ CH_2COOH; \end{matrix}$ II. $\begin{matrix} & & \diagup CH_3 \\ CH_2.C & - & OH \\ | & & \diagdown O \\ CH_2.CO. & & \end{matrix}$

Bredt showed further that acetyl-lævulinic acid does not stand alone, but that in all probability a large number of γ-ketone acids have an analogous constitution. This essentially widens our conceptions regarding the nature of ketone acids. It is evident that according to this theory two series of isomeric compounds can be predicted, the γ-ketone acids and the γ-oxy-lactones. Doubtless the atoms or atomic groups which are in combination with the α-, β- and γ-carbon atoms have the greatest influence on the lactone formation; and further investigation is necessary to determine the conditions under which the γ-ketone acid or the corresponding γ-oxy-lactone is the most stable, and under what conditions both compounds can exist.[1] If these views concerning the γ-ketone acids be extended to the γ-dicarbonic acids, as Bredt has done at the close of his paper, then the isomeric γ-dioxylactones would stand in the same relation to the γ-dicarbonic acids as the γ-oxy-lactones to the γ-ketone acids. In the formulas of the γ-dioxy-lactones, two hydroxyls are, to be sure, united to the same carbon atom, but this is also the case in chloral hydrate, mesoxalic acid, the dioxy-tartaric acids and other compounds, in all of which this carbon atom, as in the new formula for maleic acid, is united to strongly negative groups.

Assuming now that in the unsaturated lævulinic acid, which is probably L. Wolff's co-called acetacrylic acid, and which bears the same relation to lævulinic acid that ethylene bears to ethane, viz.

$\begin{matrix} & & \diagup CH_3 \\ CH.C & - & OH \\ \| & & \diagdown O \\ CH.CO & & \end{matrix}$ —assuming that in this acid it were possible to substi-

tute hydroxyl for methyl, an acid of the formula $\begin{matrix} & & \diagup OH \\ CH.C & - & OH \\ \| & & \diagdown O \\ CH.CO & & \end{matrix}$

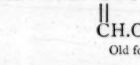
would be obtained. This would be maleic acid, if the new formula for this acid is correct.

[1] On comparing lævulinic and succinic acids, one is led to think that perhaps the two isomeric modifications of the unsaturated lævulinic acid corresponding to fumaric and maleic acids could be more easily obtained than those of lævulinic acid itself. Dr. Bredt has informed me that he has for a long time been occupied with researches in this direction.—ANSCHÜTZ.

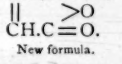
It would, on the other hand, be a very strong argument in favor of the new formula of maleic acid if we could prepare maleic acid from the unsaturated lævulinic acid, according to the method mentioned above. According to my views this was effected several years ago.

Kekulé and Strecker[1] showed that trichlorphenomalic acid is unsaturated lævulinic acid in which the hydrogen atoms of the methyl are replaced by three chlorine atoms. Trichlorphenomalic acid has, according to its description, all the peculiarities of a lactone in a higher degree than lævulinic acid. It has a pleasant odor and is volatile with water vapor. We therefore propose in place of the formula of Kekulé and Strecker for the trichlorphenomalic acid, one in which the acid appears to be the isomeric γ-oxylactone of β-trichloracetacrylic acid:

Trichlorphenomalic acid:

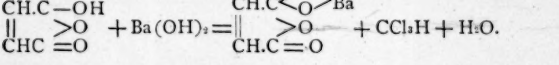


Old formula.



New formula.

On treating trichlorphenomalic acid with a solution of barium hydrate, there is formed, as Kekulé and Strecker[2] have shown, chloroform and the barium salt of maleic acid, and, according to my views, this reaction takes place in the sense of this equation:



This and other reactions of trichlorphenomalic acid are in harmony with the formula proposed by me for this acid.

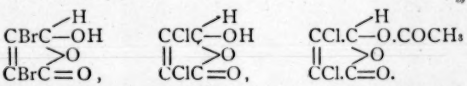
In complete harmony with this conception of the change undergone by trichlorphenomalic acid when treated with alkalies or alkaline earths are the results of the valuable researches of Hill and Sanger,[3] "On the brompyromucic acids." The principal products of the transformations of these acids are, throughout, derivatives of maleic and not of fumaric acid. In all the brompyromucic acids, the "ethylene oxide oxygen," which is required for the γ-dioxylactone formula of maleic acid, is already present.

It would lead too far should I, starting with this new formula for maleic acid, attempt an interpretation of the numerous investi-

[1]Annalen der Chemie **223**, 170. [2]Ibid. **223**, 170. [3]Ibid. **232**, 42.

gations made by Hill and Sanger.[1] I will therefore content myself by calling attention to one point.

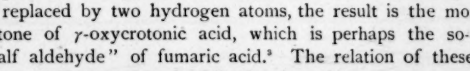
It was formerly believed that mucochloric and mucobromic acids were the substitution-products of the half aldehydes of fumaric acid, and lately, of maleic acid. It appears to me that there can be but little doubt that these substances should be represented by formulas which are analogous to those of lævulinic and maleic acids, thus:



Mucobromic acid. Mucochloric acid. Acetyl mucochloric acid.

The acetyl compound of mucochloric acid prepared by Jackson and Hill,[2] and which is evidently analogous to acetyl-lævulinic acid, speaks in favor of the correctness of the above formulas, according to which it is seen that the substances mentioned do not behave like aldehydes.

Maleic acid is therefore to be regarded as a lactone derivative of γ-oxycrotonic acid, and as the dioxylactone of this acid. If we suppose both halogens in the mucochloric or mucobromic acids to be replaced by two hydrogen atoms, the result is the monoxylactone of γ-oxycrotonic acid, which is perhaps the so-called "half aldehyde" of fumaric acid.[3] The relation of these substances is illustrated in the following formulas:



If maleic acid be indeed a γ-dioxylactone, it ought to be possible to break the lactone ring. Then, if it be further possible to retain the carboxyl formed as a result of this separation, and to add a carboxyl to the γ-carbon atom, the acid thus formed would be fumaric acid. If such a reaction is to prove anything with regard to the constitution of fumaric acid, those reagents must of course be avoided which would convert free maleic into fumaric acid. In the foregoing paper, by Mr. Wirtz and myself, the experimental solution of this problem is described, and I will now discuss the results of the investigation.

[1] Annalen der Chemie **232**, 42.
[2] This Journal **3**, 46.
[3] Limpricht, Annalen der Chemie **165**, 285.

On heating maleic anhydride with aniline there is formed, together with the anil of phenyl-aspartic acid, the anil of maleic acid, which must have one of the two following formulas:

$$\text{I.}\ \begin{matrix} CH.CNC_6H_5 \\ \| \quad >O \\ CH.CO \end{matrix}; \qquad \text{II.}\ \begin{matrix} CHCO \\ \| \quad >NC_6H_5. \\ CHCO \end{matrix}$$

In either way the maleinanil may be regarded as a derivative of maleic anhydride. On treating maleinanil with ammonia, or better with barium hydrate solution, salts of the anilic acid are formed, which, whether formula I or II be correct, has the following constitution:

$$\begin{matrix} CH.CONHC_6H_5 \\ \| \\ CH.COOH. \end{matrix}$$

The ring of maleic acid is broken, a carboxyl is formed, and it only remains to replace the aniline residue by hydroxyl. This is easily accomplished through saponification with an alcoholic solution of potassium hydrate. The product is fumaric acid. The anilic acid obtained from maleinanil must be regarded as a derivative of fumaric acid, and as fumaranil; for, to the best of our knowledge, all conditions tending to change maleic acid, if it were first formed, into fumaric acid have been avoided. Fumaric acid, therefore, in all probability contains two carboxyl groups, which view is strengthened by Claissen and Thomson's[1] synthesis of fumaric acid.

The researches of Ostwald,[2] on the electrical conductivity of fumaric and maleic, and of mesaconic and citraconic acids, are in accord with these results. To be sure, Ostwald sees in his investigations arguments in favor of the formulas of Kekulé, Swarts and Fittig for maleic and citraconic acids; but Ostwald calls attention to the similarity in the behavior of maleic acid to that of phosphorous and selenous acids, which, as he will probably freely admit, is more striking on the assumption of the dioxylactone formula for maleic acid than on the assumption of any one of the other expressions heretofore proposed. Now, as the constitution of maleic acid from a study of its chemical changes appears to a certain degree established, the investigations of the electrical

[1] Annalen der Chemie **218**, 169. [2] Journ. prakt. Chem. [N. F.] **32**, 362.

conductivity might become a very valuable aid in the determination of the constitution of dicarbonic acids.

As a conclusion to my arguments, having for their object the establishment of the dioxylactone formula for maleic acid, and the dicarboxyl formula for fumaric acid, I should like to point out some of the most important inferences that may be drawn therefrom.

Since fumaric and maleic acids are for the most part converted by oxidation into racemic and inactive tartaric acids respectively, it is very probable that racemic acid is to be regarded as a carboxyl acid, and inactive tartaric acid as a dioxylactone. Owing to the great analogy of fumaric to mesaconic acid and of maleic to citraconic acid, the corresponding acids must be analogously constituted, thus:

$$\begin{array}{l} CH_3C.COOH \\ \quad\| \\ CH.COOH, \end{array}$$

Mesaconic acid.

$$\begin{array}{l} CH_3C.C(OH)_2 \\ \quad\| \quad >O \\ CHCO, \end{array} \quad \text{or} \quad \begin{array}{l} CH.C(OH)_2 \\ \quad\| \quad >O \\ CH_3C.\ CO. \end{array}$$

Citraconic acid.

Citraconic acid could accordingly be regarded as the dioxylactone of γ-oxy-α or γ-oxy-β-methyl-crotonic acid. The theory allows two isomeric modifications of citraconic acid, and I must leave it to time to decide which of these modifications represents the known citraconic acid. The mono-substitution products and the halogen addition-products of fumaric and maleic acids may be represented by analogous formulas:

$$\begin{array}{l} CH.COOH \\ \quad\| \\ CBr.COOH, \end{array}$$

Monobromfumaric acid.

$$\begin{array}{l} CBr.C(OH)_2 \\ \quad\| \quad >O \\ CH.CO, \end{array} \quad \text{or} \quad \begin{array}{l} CH.C(OH)_2 \\ \quad\| \quad >O \\ CBr.CO, \end{array}$$

Monobrommaleic acid.

$$\begin{array}{l} CHBr.COOH \\ \quad| \\ CHBr.COOH, \end{array}$$

Ordinary dibromsuccinic acid.

$$\begin{array}{l} CHBr.C(OH)_2 \\ \quad| \quad >O \\ CHBr.CO. \end{array}$$

Isodibromsuccinic acid.

The tendency of unsaturated acids to form anhydrides increases with the replacement of the hydrogen, in union with doubly linked carbon atoms, by alkyl residues or halogen atoms. This is shown in the behavior of dibrommaleic and bromcitraconic acids.

It can now be easily understood why maleic and fumaric acids, monobrommaleic and monobromfumaric acids, citraconic and

mesaconic acids, are capable of forming only one anhydride; and why maleic and citraconic acids are so much more readily converted into anhydrides than fumaric or mesaconic acids. On the other hand, the difference in the salts, ethers and chlorides of the acids is just as easily explained.

We find, for the first time, in this dioxylactone formula for maleic acid a satisfactory explanation of the change of maleic into fumaric acid by mineral acids. Further research is necessary, however, before a satisfactory interpretation of the change of maleic acid ethers into those of fumaric acid can be given.[1] At first glance there appears to be a contradiction here, inasmuch as the treatment of the lactone-maleic acid with hydrochloric acid gives fumaric acid, while in other cases a solution of hydrochloric acid promotes the formation of lactones from oxyacids. The contradiction is, however, only apparent. The lactone ring of maleic acid, as in the case of other lactones, is capable of being broken by hydrochloric acid; the chlorine in the case of maleic acid unites with the carbon atom, with which the two hydroxyls are connected. This chlorine atom can unite to form hydrochloric acid either with the hydrogen of the neighboring hydroxyl or with the hydrogen of the carboxyl in the γ-position. The first takes place, and fumaric acid is formed according to the following equation:

$$\begin{matrix} CH.C(OH)_2 \\ \| \quad \diagdown Cl \\ CH.COOH \end{matrix} - HCl = \begin{matrix} CH.COOH \\ \| \\ CH.COOH. \end{matrix}$$

The formation of the same monobromsuccinic acid by the action of hydrobromic acid on fumaric and maleic acids is a necessary consequence of the general behavior of the halogen acids towards maleic acid.

The results of the chemical and physical investigations on fumaric and maleic acids and on their ethers accord better with the formulas proposed by me for these substances than with any of the earlier hypotheses. And it is certainly advisable to give more consideration to the physical properties than has hitherto been the custom in speculations on the constitution of organic compounds.

[1] Ber. d. deutsch. chem. Ges. **11**, 1644; **12**, 2280.—I have carried my observations further and found that the change appears to have certain limits — that is, that nearly but not quite all the maleic acid ether which is used in the reaction is changed into the corresponding fumaric acid ether. A separation of the ethers themselves involves insurmountable difficulties, and it is only because I have succeeded in finding a method of separation, depending upon the properties of the barium salts, that I hope to be able to carry the investigations to an end.—ANSCHÜTZ.

I wish especially to emphasise the fact that by the assumption of the dioxylactone formula for maleic acid, the van t'Hoff-Le Bel's formula for this acid would have to be given up. The explanation given by van t'Hoff-Le Bel concerning the relations of fumaric and racemic acids would, on the other hand, not be affected in the least by the new formula for maleic acid.

The isomerism of fumaric and maleic acids descends, to be sure, from the region of geometrical isomerism to that of ordinary isomerism. Under these circumstances it is not necessary for me to discuss the conception of alloisomerism introduced by Michael.

In the above transformations of fumaric and maleic acids I have not mentioned the formation of one succinic acid from both maleic and fumaric acids, not because I considered it difficult to give a plausible explanation of these facts on the basis of the formulas for fumaric and maleic acids defended by me, but because it seemed to me doubtful whether we have, in ordinary succinic acid, a dicarboxyl acid or a dioxylactone; and, further, the possible modification, still undiscovered, may in time be found. Besides, in the face of the evident influence which the atoms and atomic groups in union with the α- and β-carbon atoms exert on the behavior of both hydroxyl groups, I am far from assuming that the isomers corresponding to fumaric and maleic acids of every γ-dicarbonic acid can be isolated.

These considerations show that, among the methods of formation and transformation of fumaric and maleic acids, not one is inconsistent with the assumption of the dioxylactone formula for maleic acid. I even venture to assert that in the light of the earlier views concerning the isomerism of fumaric and maleic acids, the reactions described by me—viz. the formation of maleic acid from trichlorphenomalic acid; the formation of bromine derivatives of maleic acid from the bromine derivatives of the furfuran group; the formation of fumaric acid from maleinanil—cannot be understood at all, or only by the aid of less probable assumptions.

It would be a simple matter to apply to a greater extent than has been done in this paper, the consequences resulting from a consideration of the dioxylactone formula, to those isomeric dicarbonic acids which show differences of behavior similar to those of fumaric and maleic acids. I have, however, omitted such a generalisation, believing it better to wait till other investigations

have proved that the isomerism of any two dicarbonic acids is of a nature similar to that of fumaric and maleic acids. Investigations of this kind have for some time been in progress in this laboratory on the isomeric camphoric, dimethylsuccinic, diphenylsuccinic acids, etc. Above all, researches undertaken by Mr. Bendix and myself on the diphenylsuccinic acids, as well as on diphenylmaleic anhydride, seem to me to be of especial interest. If indeed the isomerism of both diphenyl-succinic acids is of the same nature as that of fumaric and maleic acids, then it would be *proved* that the difference between these latter acids cannot possibly be ascribed to the existence in one of these acids of a carbon atom with two free bonds, as this is impossible in the case of diphenylsuccinic acids.

BONN, *March* 20, 1887.

ON A COMPOUND OF MANGANESE SESQUIOXIDE WITH CUPRIC OXIDE.

BY E. A. SCHNEIDER.

The compounds of the sesquioxides of aluminium, chromium, and iron with basic oxides have already been prepared by many different methods. I have searched the chemical literature in vain for a description of compounds in which either manganese sesquioxide acts as an acid toward the oxides with strongly basic properties, or the oxides of copper, silver, and mercury as bases towards the sesquioxides in general.[1] This fact, in connection with the well-known properties of these oxides, properties which indicate an analogy on the one hand between manganese sesquioxide and the sesquioxides of iron, chromium, and aluminium, and on the other hand between the oxides of copper, silver, and mercury and those of the alkali metals, led me to think that compounds of the kind referred to might be made.

Many compounds of metallic oxides are known, among which may be mentioned the aluminates and analogous compounds of iron and chromium. As is well known, the principal representatives of the group of aluminates, the spinels, are to be regarded

[1] I have found two compounds mentioned belonging to the latter class. $CuOFe_2O_3.5HO$ is mentioned in Frémy's Encyclopédie chimique, but without naming the original article; $CuO.Cr_2O_3$ is described by Gerber, Bull. de la Soc. chim. **27**, 435.

as salts of the acid AlO.OH. Thus spinel itself is $(AlO.O)_2Mg$ or $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Mg$; similarly, cymophane is $(AlO.O)_2Be$; hercinite is $(AlO.O)_2Fe$. These have been made artificially by Ebelmen.[1] Chromite is an analogous compound and is represented by the formula $(CrO.O)_2Fe$.

Gerber[2] obtained compounds of chromic oxide with the oxides of calcium, barium, magnesium, iron, zinc, and copper. The reaction which he used consisted in heating to red heat a mixture of potassium bichromate with an anhydrous metallic chloride: $MCl_2 + K_2Cr_2O_7 = 2KCl + (CrO.O)_2M + 3O$. In this equation M represents a bivalent metal.

Zincates and cuprates of the strong bases have also long been known. Thus Berzelius described a zincate, $ZnO.K_2O = Zn(OK)_2$; and Frémy[3] one of the composition $2ZnO.K_2O = \begin{matrix}Zn\\Zn\end{matrix}\!\!<\!\!\begin{matrix}OK\\O\\OK.\end{matrix}$

Loew[4] described a very unstable compound, $CuO.Na_2O = Cu(ONa)_2$.

Taking into account the statement of Berzelius that the existence of zincates of the alkaline earth metals is probable, and the negative results which I obtained in trying to prepare analogous compounds of copper, I concluded that the acid properties of zinc oxide are far stronger than those of cupric oxide. Considering on the other hand the more basic than acid properties of cupric oxide; further, the fact that chromic oxide and ferric oxide combine with cupric oxide, and that, in the natural arrangement of the elements according to Mendelejeff, manganese occupies the place between chromium and iron, I concluded that manganese sesquioxide would also in all probability combine with cupric oxide. The experiment has confirmed this supposition.

None of the previously mentioned reactions seemed to me to be adapted to my purpose. The application of high temperatures was entirely excluded, as cupric oxide and manganese sesquioxide are changed at a high heat. The reaction of Pelouze (precipitation of a mixture of manganous chloride and copper chloride in certain molecular proportions by an excess of potash) did not promise to be of much use. More promising appeared to me a

[1] Ann. Chim. Phys. [3] **22**, 213; **33**, 34.
[2] Comptes rendus **15**, 1106.
[3] Bull. Soc. chimique **27**, 435.
[4] Zeitschrift f. an. Chemie **9**, 463.

reaction which Berzelius[1] mentions in a paper on zinc oxide. He states that Sander had obtained a zincate of alumina or an aluminate of zinc by mixing a solution of alumina in caustic potash with zinc oxide ammonia.

Now I had noticed, when experimenting with the blue solution which results from the treatment of copper with ammonia in presence of air, and which is commonly though wrongly called copper oxide ammonia, how very slowly cupric hydrate is precipitated from it by caustic alkalies, even in very dilute solutions.

To 50 cc. of such a solution containing 0.4906 gram CuO I added 100 cc. caustic soda (sp. gr. = 1.4) and 500 cc. water. After standing ten days at ordinary temperature a considerable precipitate had formed, but the solution still remained blue.

This behavior of copper salts towards caustic alkalies in ammoniacal solution seemed to me very favorable for the purpose of testing the affinity of manganese sesquioxide towards cupric oxide.

Manganous hydroxide is instantly thrown down from solutions of manganous salts by caustic alkalies. By the access of air the manganous compound is changed to the manganic compound. If now this reaction is carried out in presence of a copper salt in ammoniacal solution, and if a strong affinity exists between copper oxide and manganic oxide, the former must also be instantly precipitated and combine with the manganic oxide.

I used the following solutions in my experiments:

1. The blue solution which is obtained by repeatedly pouring ammonia over copper scraps in presence of air. According to Peligot,[2] this solution is not copper oxide ammonia, as commonly supposed, but it contains a salt of the composition $Cu(NO_3)_2 2NH_3 + 2H_2O$, a double compound of nitrite of copper and ammonia. Submitted to a temperature of 100° this salt loses ammonia and water until copper nitrite, $(NO_2)_2Cu$, remains behind.

The solution which I have employed contained 13.8960 grams CuO per liter.

2. A solution of manganous chloride containing 36.33 grams Mn_2O_3 per liter.

3. Caustic potash (sp. gr. = 1.2).

[1] Ann. der Chemie **9**, 181.

[2] Ann. Chim. Phys. [3] **63**, 343.

First Series of Experiments.

Four portions of the ammoniacal copper salt solution representing respectively 1, 2, 3 and 4 molecules of CuO were mixed each with 100 cc. of the caustic potash. To each portion a quantity of the solution of manganous chloride, representing in each case one molecule of Mn_2O_3, was added at once. After the lapse of one hour, during which the mixtures were frequently stirred, they were diluted with water to about 500 cc., frequently decanted, and the precipitate brought on a filter and washed with hot water until the wash water no longer showed an alkaline reaction.

1. In the case in which the solution contained 1 mol. Mn_2O_3 to 1 mol. CuO the results were as follows:

After addition of the manganous chloride the deep blue solution instantly became colorless and a black precipitate settled to the bottom.

2. With the proportion 1 mol. Mn_2O_3 to 2 mol. CuO the results were the same as in 1.

3. With the proportion 1 mol. Mn_2O_3 to 3 mol. CuO the supernatant liquid appeared, after the same lapse of time which solutions 1 and 2 had been allowed to stand, deep blue.

The precipitate formed in this case was dried to a constant weight at 100° C., and afterwards heated over a Bunsen burner until no further loss in weight took place. It was then dissolved in hydrochloric acid, the copper precipitated with hydrogen sulphide, and the manganese determined in the filtrate by precipitating as carbonate and weighing as the oxide Mn_3O_4. The manganese found in this way, calculated on the basis of the precipitate dried at 100°, corresponded to 50.38 per cent. Mn_2O_3, and calculated on the basis of the precipitate heated to a high temperature it corresponded to 50.71 per cent. Mn_3O_4.

4. With the proportion 1 mol. Mn_2O_3 to 4 mol. CuO the supernatant liquid remained deep blue. The precipitate dried at 100° contained an amount of manganese corresponding to 43.47 per cent. Mn_2O_3, and when heated to a high temperature the manganese corresponded to 44.18 per cent. Mn_3O_4.

All the precipitates were black, and acquired a brownish tinge after being dried at 100° C. They dissolved in chlorhydric acid, with evolution of chlorine, even before being dried. As a compound of the composition $Mn_2O_3.2CuO$ contains 49.87 per cent. Mn_2O_3

(Mn = 55, Cu = 63.4), the results of experiment No. 3 led me to believe that manganese sesquioxide combines with only two molecules of cupric oxide. The results of experiment No. 4 suggested a slight modification in order to ascertain the maximum of cupric oxide that can combine with manganese sesquioxide. Instead of adding the manganous chloride all at once, I allowed it to drop very slowly into the mixture of the ammoniacal copper salt and caustic potash, and kept the mixture constantly stirred. The precipitates obtained in this way contained a quantity of manganese corresponding very nearly to the formula $Mn_2O_3.3CuO$.

Second Series of Experiments.

1. When the solution contained 1 mol. Mn_2O_3 to 3 mol. CuO the supernatant liquid was pale blue.

The precipitate, after being heated to a high temperature, contained a quantity of manganese corresponding to 44.21 per cent. Mn_3O_4.

2. Proportion 1 mol. Mn_2O_3 to 3 mol. CuO. The supernatant liquid was of a pale blue color. The precipitate dried at 100° contained 44.06 per cent. Mn_2O_3, and heated to a high temperature it contained 44.42 per cent. Mn_3O_4.

3. Proportion 1 mol. Mn_2O_3 to 4 mol. CuO. The supernatant liquid was deep blue. The precipitate dried at 100° contained 40.28 per cent. Mn_2O_3 and 54.54 per cent. CuO (total, 94.82 per cent.); heated to a high temperature it contained 40.96 per cent. Mn_3O_4 and 57.45 per cent. CuO (total, 98.45 per cent.).

4. Proportion 1 mol. Mn_2O_3 to 5 mol. CuO. The supernatant liquid was deep blue. The precipitate dried at 100° contained 40.02 per cent. Mn_2O_3 and 56.51 per cent. CuO (total, 96.53 per cent.); heated to a high temperature it contained 41.63 per cent. Mn_3O_4 and 59.08 per cent. CuO (total, 100.71 per cent.).

It will be seen from the above results that the composition of the precipitate approaches very nearly that of a compound $Mn_2O_3.3CuO$ which requires 39.88 per cent. Mn_2O_3 and 60.12 per cent. CuO. From experiments 3 and 4 it is further clear that an excess of at least 1 or 2 molecules of cupric oxide above that required by theory favors the formation of the compound $Mn_2O_3.3CuO$. The considerable deficit in the summation of the analyses, particularly of the precipitates dried at 100°, is to be

ascribed to water, which apparently requires a higher temperature for complete expulsion, and also to silica, as I had omitted to purify the caustic potash by alcohol.

I have made two more experiments with an ammoniacal solution of cupric chloride and the same solutions of manganous chloride and caustic potash.

This time I did not work with previously determined quantities of the reagents, but added the manganous chloride solution drop by drop to a concentrated ammoniacal solution of cupric chloride which was previously mixed with an excess of caustic potash. The addition of manganous chloride was stopped when the liquid was still deep blue, and the precipitate then filtered off and analysed in the usual way. The strongly ignited precipitates contained (1) 49.40 per cent. CuO, and (2) 53.43 per cent. CuO.

A larger number of experiments will no doubt throw light on the question which copper salt is best adapted to the reaction.

I have performed similar experiments qualitatively with ammoniacal solutions of silver oxide and of zinc oxide, and have found that silver oxide combines with manganese sesquioxide, but that zinc oxide does not.

It is a pleasant duty for me to thank Professor E. W. Hilgard for the kind permission to use the laboratory which is under his direction.

Berkeley, University of California.

RESEARCHES ON ALLOISOMERISM.

II.

By A. Michael and G. M. Browne.

It is in the compounds of the butyl series that those instances of isomerism and peculiar properties of certain derivatives, that cannot be explained by the present theories of structural chemistry, are first shown in a marked degree. The properties of the α- and β-hydroxy-fatty acids stand in a close relation to their structural formulae; but the instability of the γ-hydroxy-acids is a fact before which the present theories stand perfectly helpless in offering an

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explanation. There is no doubt that the explanation will be found in the atomic grouping of the molecule in space; and, as the derivatives of the higher series of fatty compounds are those that particularly show these apparently anomalous properties, it is through their investigation that our knowledge of atomic grouping in space must be gained. A class of compounds that very noticeably show a relation to grouping in space are the crotonic acids and their halogen derivatives, and the correct interpretation of their constitution is certain to have considerable influence on the chemical theories of the structure of organic compounds.

The difficulty in classifying the crotonic acids begins in the formation of the solid acid from allyl cyanide. According to this synthesis it should have the constitution $CH_3-CH-CH_2-COOH$, and indeed it was universally assigned to it[1] until Kekulé[2] showed that its behavior towards fused alkalies would not admit of this constitution, but agreed with $CH_3-CH-CH-COOH$. An explanation has been offered by Pinner,[3] but the subject can hardly be considered as on a satisfactory basis. A second crotonic acid was discovered by Geuther[4] in 1871. This chemist obtained two isomeric chlorcrotonic acids by the action of phosphorus pentachloride on acetacetic ether, and the reduction of β-chlorisocrotonic acid gave a liquid crotonic acid, while the β-chlorcrotonic acid gave the solid acid. The constitutions generally adopted for these acids are $CH_3-CCl-CH-COOH$ for β-chlorcrotonic acid, $CH_2-CCl-CH_2-COOH$ for β-chlorisocrotonic acid, and $CH_2-CH-CH_2-COOH$ for isocrotonic acid, although the formation of a compound represented by the adopted constitution of β-chlorisocrotonic acid is contradictory to all our knowledge concerning the splitting off of a halhydric acid from an organic halogen acid. A third chlorcrotonic acid has been obtained by the reduction of trichlorbutyric acid, and undoubtedly has the constitution $CH_3-CH-CCl-COOH$.[5]

A different conception of the constitution of the acids obtained by Geuther is due to van't Hoff,[6] who considered both the chloro-

[1] Lwow, Berichte d. deutsch. chem. Gesell. **3**, 96; Paterno and Amato, Comptes rendus **69**, 479; Claus, Berichte d. deutsch. chem. Gesell. **3**, 181; Erlenmeyer, Lehrbuch, 3:2; Tollens, Zeitschrift für Chemie, 1871, 253; Rinne and Tollens, Annalen der Chemie **159**, 105.

[2] Berichte d. deutsch. chem. Gesell. **3**, 608; Annalen der Chemie **162**, 114.

[3] Berichte d. deutsch. chem. Gesell. **12**, 2053.

[4] Zeitschrift für Chemie, 1871, 242; Geuther and Frölich, ibid. 1869, 270.

[5] Krämer and Pinner, Annalen der Chemie **158**, 37; Sarnow, ibid. **164**, 93; Friedrich, ibid. **219**, 368.

[6] La Chimie dans l'espace.

acids formed in the action of phosphorus pentachloride on acetacetic ether as having the constitution $CH_3 - CCl - CH - COOH$, and isocrotonic acid as having the same constitution as solid crotonic acid. This view has been in some degree corroborated by the experiments of Friedrich,[1] who found that the chloro-acids gave the same ethoxy-acid when heated with sodium ethyl oxide; and by C. Kolbe,[2] who made the interesting observation that isocrotonic acid on treatment with bromine gave the $\alpha\beta$-dibrombutyric acid that had been obtained in the same way from solid crotonic acid. On the other hand, Autenrieth[3] has very recently obtained isomeric phenylmercapto-crotonic acids by treating the chloro-acids with sodium phenyl sulphide; facts, however, that do not speak against the van't Hoff constitutional formulae. It is also worthy of note that Hemilian[4] found that isocrotonic acid can be converted by heating into solid crotonic acid, and Friedrich[5] that β-chlorcrotonic acid can be converted in the same way into β-chlorisocrotonic acid. The mono-bromo-derivatives of crotonic acids are represented by two acids. An alpha-acid has been obtained by decomposing α-dibrombutyric acid with alkalies, and an isomeric acid by treating $\alpha\beta$-dibrombutyric acid in the same manner.[6] In order to explain this isomerism the second acid was given the constitution $CH_3 - CBr - CH - COOH$, which structural formula, though universally adopted, had no further proof than the fact that the isomerism of the two acids could be explained by the assumption.[7]

In the present paper we have endeavored to bring conclusive proofs that the generally accepted constitutions of β-chlorisocrotonic and so-called β-bromcrotonic acids cannot be longer upheld, and we also have been able to obtain a second α-chlorcrotonic and a β-bromcrotonic acid.

[1] Annalen der Chemie **219**, 322.
[2] Journal f. prak. Chemie [2] **25**, 396.
[3] Berichte d. deutsch. chem. Gesell. **20**, 1531.
[4] Annalen der Chemie **174**, 328.
[5] Ibid. **219**, 363.
[6] Michael and Norton, this Journal **2**, 15; also Erlenmeyer and Müller (Berichte d. deutsch. chem. Gesell. **15**, 49), who subsequently showed that a small amount of alpha-acid is formed at the same time.
[7] That the importance of these observations was not overlooked will be seen from the following extract: "The formation of different bromcrotonic acids from α- and $\alpha\beta$-dibrombutyric acids presents considerable interest, as Tollens has shown that the α- and $\alpha\beta$-dibrompropionic acids yield the same bromacrylic acid. Our results, in thus characterising an important difference in the properties of substitution products of propionic and butyric acids, indicate that a more thorough and systematic investigation than has hitherto been made of the substitution products of the fatty acids will show further marked differences in the properties of these acids; results which would contribute in no small measure to a better insight into the relations and nature of homologous organic compounds." This Journal **2**, 20.

Addition of Bromhydric Acid to Tetrolic Acid.

If the bromcrotonic acid obtained from $a\beta$-dibrombutyric acid is the β-derivative of solid crotonic acid, its synthesis should be realised by the addition of bromhydric acid to tetrolic acid, as the halogen in these reactions always takes the β-position towards the carboxyl, and besides it has been proved that tetrolic and chlorhydric acids unite to form β-chlorcrotonic acid.[1]

In preparing bromcrotonic acid from tetrolic acid it is necessary to start from the latter acid in a perfectly pure state. Our first experiments were made with an acid that had the correct melting point, but gave a faint trace of halogen when heated in a flame with copper oxide. This acid was sealed in a tube with a large excess of bromhydric acid (saturated at 0°), and kept cool for about a day. On addition of water to the solution, long white needles separated that in a crude state melted from 75°–83°; after several crystallisations from water, at 83°–85°; but repeated crystallisation from ligroin brought the substance to the constant melting point of 94°–95°. The bromine estimations of this apparently pure substance gave results that were over one-half per cent. less than that indicated by theory, and a silver estimation of the silver salt came somewhat more than two per cent. higher than the theoretical percentage. It seems very probable from these results that the chlorcrotonic acid contained in the tetrolic acid has very nearly the solubility of the bromcrotonic acid formed in the reaction, and cannot be separated from it by crystallisation.

The difficulty is obviated by starting with perfectly pure tetrolic acid, and we found that working according to the following directions gave the most satisfactory results: A mixture of one part of tetrolic acid and five parts of bromhydric acid, saturated at 0°, is sealed in a glass tube, placed on ice for about five hours, and then allowed to stand at ordinary room-temperature for two or three days. It was noticed that tetrolic acid dissolves immediately in bromhydric acid, and that after several hours long needles begin to separate from the solution. The contents of the tube is mixed with an equal volume of water, cooled off in ice, and the precipitate separated by filtration. The precipitate melted from 75°–83°; repeated crystallisation from water failed to raise the melting point above 85°, but after crystallising it four times

[1] Friedrich, Annalen der Chemie **219**, 370.

from ligroin it melted constantly at 94.5°–95°. The analyses of this product gave the following figures:

0.3606 gram substance dried in a vacuum gave 0.3829 gram CO_2 and 0.1116 gram H_2O.

0.2193 gram substance dried in a vacuum gave 0.2517 gram AgBr.

	Theory for $C_4H_5BrO_2$.	Found.
C	28.96	29.09
H	3.43	3.03
Br	48.84	48.48

The new bromcrotonic acid crystallises from water as cuneated plates; from ligroin in firm feathery needles that melt at 94.5°–95°. It is sparingly soluble in cold, pretty soluble in hot water, and separates from its warm aqueous solution on cooling as an oil that solidifies on standing. In cold ligroin it is sparingly soluble, but readily soluble in cold benzene, carbon bisulphide, acetic ether, acetic acid, ether, alcohol, and chloroform. Treated with steam the acid passes over with difficulty. The formation of this acid is represented by the following equation:

$$CH_3-C-C-COOH + HBr = CH_3-CBr-CH-COOH.$$

The potassium salt was obtained by neutralising an aqueous solution of the acid with pure caustic potash, and allowing the solution to evaporate by exposure to the air until most of the salt had separated. It is filtered from the mother liquor, washed with alcohol, and dried by exposure to the air. The salt crystallises as thin plates that are readily soluble in cold water and do not contain water of crystallisation.

0.8140 gram air-dried salt did not lose in weight when heated to 100°, and gave 0.3469 gram K_2SO_4.

	Theory for $CH_3-CBr-CH-COOK$.	Found.
K	19.13	19.21

The silver salt was made by precipitating an aqueous solution of the potassium salt with silver nitrate, filtering the precipitate, and crystallising it from water. It crystallises in thin white, almost opaque plates that are moderately sensitive to the action of light. It does not contain water of crystallisation.

0.4107 gram air-dried salt did not change its weight at 100°, and gave 0.288 gram AgBr.

	Theory for $CH_3-CBr-CH-COOAg$.	Found.
Ag	39.70	40.33

The barium salt was obtained by adding an excess of barium carbonate to an aqueous solution of the acid, allowing the mixture to stand for an hour, filtering, and concentrating the filtrate by evaporation at ordinary temperature. It crystallises in colorless plates and prisms that are readily soluble in water and insoluble in hot absolute alcohol. They contain one molecule of water of crystallisation.

0.4285 gram air-dried salt lost 0.0172 gram H_2O at 100°.
0.5768 gram air-dried salt gave 0.2812 gram $BaSO_4$.
0.5078 gram air-dried salt gave 0.2465 gram $BaSO_4$.
0.3422 gram salt dried at 100° gave 0.1742 gram $BaSO_4$.

	Theory for $(CH_2-CBr-CH-COO)_2Ba.H_2O$.	Found.	
H_2O	3.73	4.01	
Ba	28.36	28.66	28.56

	Theory for $(CH_2-CBr-CH-COO)_2Ba$.	Found.
Ba	29.46	29.89

The properties of the three known bromcrotonic acids are given below in tabular form.

α-Acid.	*αλ-α-Acid (old β).*	*β-Acid.*
From $CH_3-CH_2-CBr_2-COOH$.	From $CH_3-CHBr-CHBr-COOH$.	From $CH_2-C-C-COOH$ and HBr.
Long needles (from water). Needles that can be easily pulverised (from ligroin).	Long needles. Needles that can be easily pulverised.	Cuneated plates. Firm feathery crystals that can only be pulverised with difficulty.
Melting point 106.5°.	90° (C. Kolbe). 92° (Michael and Norton).	94.5°–95°.
Silver Salt.		
White needles. Stable towards light.	White needles. Very sensitive to light. Cannot be crystallised from water without decomposition.	Thin plates. Moderately sensitive to light. Can be crystallised from water.
Barium Salt.		
Plates, with two molecules of water of crystallisation.	Plates, with 3½ molecules of water of crystallisation.	Prisms, with one molecule of water of crystallisation.

It semed possible to obtain a second β-bromcrotonic acid by allowing phosphorus pentabromide to act on acetacetic ether; as, if the reaction takes place analogously to that of the pentachloride on the ether, a mixture of two β-acids should be formed. To 50 grams acetacetic ether 330 grams powdered pentabromide were gradually added. The liquid, which had a deep violet color, was poured in small portions into cold water, and the solution shaken out with ether. After evaporating the ether the residue was treated with steam, but the quantity of acid that passed over was

too small to permit its investigation. The residue remaining after steaming was crystallised from water, and then six times from ligroin, when it gave a constant melting point of 85°. A bromine estimation of the acid gave 29.13 per cent. bromine, a result that showed the reaction had not taken place in the way that was expected, as bromcrotonic acid contains 48.8 per cent. of bromine. The product was not further examined.

Behavior of αβ-Dibrombutyric Ethylether towards Alkalies.

The observation made by one of us that αβ-dibromhydrocinnamic acid when decomposed by alkalies gives a different result from that given by the ether of the acid[1] led us to examine the bromcrotonic acid formed by decomposing αβ-dibrombutyric ether with alkalies. In decomposing αβ-dibrombutyric acid about nine-tenths of the bromcrotonic acids formed consists of allo-α-acid (old β-acid), and the remaining tenth of α-acid.

The ether was made by saturating a solution of one part of αβ-dibrombutyric acid in three parts of absolute alcohol with dry chlorhydric acid, at first without outward cooling, and then cooling at 0°. After standing twenty-four hours the liquid was poured into cold water, the mixture extracted with ether, and the ethereal solution, after shaking out with aqueous sodium carbonate, dried over calcium chloride. On evaporation of the ether the residue was distilled in a vacuum (30 mm. pressure, bath at 160°), when the greater part passed over from 110°–115°, and several fractionations under the same conditions of pressure gave an oil boiling constantly at 113°–114°. The analysis of this oil gave figures as follows:

0.1780 gram oil gave 0.2405 gram AgBr.

0.2132 gram oil gave 0.2893 gram AgBr.

	Theory for $CH_3-CHBr-CHBr-COOC_2H_5$.	Found.	
Br	58.39	57.50	57.74

[1] These observations, which I made about a year ago, have never been published. According to Glaser (Annalen der Chemie **154**, 146), allo-α-bromcinnamic acid is formed in the decomposition of αβ-dibromhydrocinnamic acid in much greater proportion than the α-acid. In making bromcinnamic acids from αβ-dibromhydrocinnamic ether I noticed that the relative proportions of bromcinnamic acids that are formed are reversed. In this case the α-acid forms the principal product, while the allo-α-acid is formed in much smaller quantity. These facts explain why the ether can be used to greater advantage for preparing phenylpropiolic acid than the acid.—A. M.

The ether forms a colorless heavy oil that boils in a vacuum (30 mm., oil-bath 150°) without decomposition at 113°. The ether was dissolved in a small amount of alcohol, and alcoholic caustic potash (one molecule of ether to two molecules of alkali) added. A violent reaction took place, and an immediate deposition of potassium bromide was noticed. After heating several minutes on a water-bath the alcohol was evaporated, and the residue extracted with cold absolute alcohol. It was filtered, the precipitate dissolved in water, and the solution acidulated and extracted with ether. On evaporation of the ether a large amount of nearly pure α-bromcrotonic acid was left. After one crystallisation it gave the correct melting point (106°). The absolute alcoholic extract contained a small amount of a potassium salt, but whether any $\alpha\lambda$-α-bromcrotonic is formed from $\alpha\beta$-dibrombutyric ether we are unable at present to ascertain. The experiment will be repeated on a larger scale with this object in view. It is certain, however, that α-bromcrotonic acid is the main product of the reaction, a result which is exactly the reverse of that obtained in decomposing the free acid.

Addition of Chlorine to Solid Crotonic Acid.

The behavior of solid crotonic acid towards chlorine was examined by Friedrich,[1] who passed the dry gas into the acid, and obtained a liquid addition product that could not be brought into a solid state. No analyses of the product are given. As Friedrich noticed the formation of chlorhydric acid in the operation, the reaction was evidently too energetic, and we therefore used a solution of the acid in carbon disulphide. We experienced, however, considerable difficulty in ascertaining the proper conditions, as will be noticed from the following experiments.

Five grams crotonic acid were dissolved in four hundred grams carbon bisulphide, and the solution saturated by a slow current of dry chlorine, an operation that took about five hours. A portion of this solution was heated on a water-bath until the carbon bisulphide was expelled, and the residue was found to consist of unchanged crotonic acid. A second portion was exposed to sunlight for a few hours, when a slight addition took place, but the greater part of the crotonic acid remained unchanged. The remainder of

[1] Annalen der Chemie **219**, 368.

the solution was allowed to stand in the cold for a day, and the bisulphide then evaporated. The residue melted at 59°–60°, and after repeated crystallisation from ligroin at 60°–60.5°. A chlorine estimation of this product gave 35.42 per cent. Cl, which is nearly ten per cent. below the calculated chlorine of dichlorbutyric acid. Three grams crotonic acid were dissolved in one hundred grams chloroform, and the solution saturated with chlorine. After four days the chloroform was evaporated, but the residue remained an oil, and could not be purified by fractionation. Three grams acid in one hundred grams chloroform and four and a half grams iodine were treated with chlorine until saturation. Iodine trichloride separated, and apparently did not act on the acid.

A solution of five grams crotonic acid in four hundred grams carbon bisulphide was cooled to —17°, and saturated with chlorine at that temperature. After standing a week in a cool place a portion was worked up, and gave a solid product melting at 57.5°–58°, and containing 43.69 per cent. Cl (theory 45.22). The remainder was again saturated with chlorine at —17° and allowed to stand several days. In this manner we obtained a product melting at 63° and consisting of pure dichlorbutyric acid.

We give the following directions as the results of our experience in preparing the acid. Ten grams crotonic acid are dissolved in four hundred grams dry carbon bisulphide, the solution cooled in a mixture of ice and salt, and saturated with dry chlorine. It is kept in a cool place for three days, then resaturated with chlorine under the same conditions, allowed to stand several days, and the carbon bisulphide evaporated by heating on a water-bath. There remains a thick heavy oil which contains a considerable amount of chloride of sulphur. The mass is treated with an excess of aqueous sodium carbonate, the solution filtered, and then, after acidifying, extracted with ether. The ethereal solution is dried over calcium chloride, and leaves, on evaporating the ether, a thick oil that deposits prismatic crystals on standing. These are separated by filtration, crystallised once from ether and several times from ligroin.

0.2672 gram acid gave 0.4854 gram AgCl.

	Theory for $CH_3-CHCl-CHCl-COOH$.	Found.
Cl	45.22	44.92

The acid crystallises in thick white prisms that are somewhat

deliquescent and melt at 63°. It is very soluble in benzene, ether, chloroform, carbon bisulphide, and hot ligroin, sparingly soluble in cold ligroin and cold water. It is evident that Friedrich worked with an impure acid.

Behavior of αβ-Dichlorbutyric Acid towards Alkalies.

The acid was dissolved in a small amount of alcohol, and an alcoholic solution of caustic potash (one molecule of acid to two molecules of base) gradually added. The reaction is energetic, but the solution was kept below 40° C. by cooling. After the solution became neutral it was mixed with water, acidified, and extracted with ether. The extract, after drying over calcium chloride, was heated on a water-bath until the ether was expelled, and the residue on cooling solidified to a crystalline mass. This was purified by crystallisation from water and ligroin, and gave the following results on analysis:

0.2348 gram substance gave 0.3481 gram CO_2 and 0.1018 gram H_2O.

0.2113 gram substance gave 0.3141 gram CO_2 and 0.0930 gram H_2O.

0.2285 gram substance gave 0.2728 gram AgCl.

0.2159 gram substance gave 0.2574 gram AgCl.

	Theory for $CH_3-CH-CCl-COOH$.	Found.			
C	39.83	40.43	40.54		
H	4.15	4.81	4.89		
Cl	29.46			29.53	29.48

The new chlorcrotonic acid crystallises from water, ligroin, or ether in fine needles that melt at 67°. It is readily soluble in hot, sparingly in cold ligroin. In warm water it is readily, in cold moderately soluble, but more so than any of the three isomeric chlorcrotonic acids, as is evident from the following determinations of solubilities:

12 grams of a saturated aqueous solution of the new acid at 19° required 75.7 cc. of caustic potash solution containing 0.0004817 gram KOH in a cc.

12.55 grams of a saturated aqueous solution of α-chlorcrotonic acid (97°) at 19° required 25.6 cc. of caustic potash solution containing 0.0004817 gram KOH in a cc.

12.1 grams of a saturated aqueous solution of β-chlorisocrotonic acid (59°) at 19° required 22.6 cc. of caustic potash solution containing 0.0004817 gram KOH in a cc.

From these results the following solubilities were calculated:

15.3 grams water at 19° dissolve one gram new chlorcrotonic acid.

47.1 grams water at 19° dissolve one gram α-chlorcrotonic acid.

52.4 grams water at 19° dissolve one gram β-chlorisocrotonic acid.

It will be noticed that the new acid is above three times more soluble in water than either of the two isomeric acids, and it is more soluble than the fourth isomeride, as that acid dissolves in 44 parts of water at 12.5°.[1]

To obtain the potassium salt an aqueous solution of the acid was neutralised with caustic potash, and the solution evaporated by standing in the air. The crystals were filtered, washed with absolute alcohol, and dried by exposure to the air. It is easily soluble in water, moderately in absolute alcohol, and crystallises from that solvent in concentric groups of fine needles. The salt does not contain water of crystallisation.

0.4318 gram salt dried by exposure to the air underwent no change in weight at 100°, and gave 0.2352 gram K_2SO_4.

	Theory for $CH_3-CH-CCl-COOK$.	Found.
K	24.60	24.45

The barium salt was made by neutralising an aqueous solution of the acid with barium carbonate, and evaporating the filtered solution at ordinary temperature on the air. It is a white crystalline salt that is easily soluble in water, but slightly soluble in alcohol, and contains three and a half molecules of water of crystallisation.

0.6922 gram air-dried salt lost 0.0976 gram H_2O at 125° C.

0.5946 gram salt dried at 125° gave 0.3678 gram $BaSO_4$.

	Calculated for $(CH_3-CH-CCl-COO)_2Ba.3H_2O$.	Found.
H_2O	14.35	14.10

	Calculated for $(CH_3-CH-CCl-COO)_2Ba$.	Found.
Ba	36.43	36.37

By adding a solution of lead nitrate to a solution of the potassium salt a crystalline precipitate was deposited that was

[1] Kahlbaum, Berichte d. deutsch. chem. Gesell. **12**, 2339.

crystallised from water. It forms white, vitreous, prismatic needles or short prisms that are somewhat soluble in water and contain one molecule of water of crystallisation.

0.3063 gram salt dried by exposure to the air lost 0.116 gram H_2O at 100° C.

	Theory for $(C_4H_4ClO_2)_2Pb.H_2O$.	Found.
H_2O	3.87	3.78

0.2947 gram salt dried at 100° C. gave 0.2002 gram $PbSO_4$.

	Calculated for $(C_4H_4ClO_2)_2Pb$.	Found.
Pb	46.41	46.43

On addition of silver nitrate to a solution of the potassium salt, a silver salt is precipitated as a white amorphous compound that is somewhat soluble in water, and not very stable on exposure to light.

The sodium salt, obtained by neutralising the acid with caustic soda and evaporating, forms small prismatic needles that are easily soluble in alcohol.

A solution of copper sulphate added to a solution of the potassium salt gives a precipitate of greenish-blue, concentrically grouped prisms that are difficultly soluble in water.

Behavior of αβ-Dichlorbutyric Ether towards Alkalies.

It seemed of interest to ascertain whether the ether of αβ-dichlorbutyric acid would yield on treating with alkalies the same chlorcrotonic acid as the free acid; or whether, as is the case with the dibrombutyric and hydrocinnamic acids, an isomeric alpha-acid would be formed in the reaction.

Pure αβ-dichlorbutyric acid in absolute alcoholic solution was saturated with dry chlorhydric acid. The solution was then allowed to stand about twelve hours, thrown into cold water, and extracted with ether. The ethereal solution was extracted with a dilute solution of sodium carbonate, dried over calcium chloride, and, after evaporation of the ether on a water-bath, fractionated in a vacuum. In this manner a colorless oil was separated that boiled under 35 mm. pressure at 96° (oil-bath at 145°).

0.2312 gram ether gave 0.3581 gram AgCl.

	Theory for $CH_3-CHCl-CHCl-COOC_2H_5$.	Found.
Cl	38.91	38.30

A portion of dichlorbutyric ether was dissolved in alcoholic potash, in the proportion of one molecule ether to two molecules alkali, and the solution allowed to stand in the cold for three or four hours. It was then worked up in the manner already described in the decomposition of dibrombutyric ether, and the chlorcrotonic acid obtained in this way consisted of the α-acid melting at 97°–98°.

We meet in this case the same remarkable difference in the behavior of $\alpha\beta$-dichlorbutyric acid and its ether towards alkalies as already proved with the corresponding bromo-compounds. While free $\alpha\beta$-dichlorbutyric acid and alkalies give an α-chlorcrotonic acid melting at 67°, the ether of the same acid when decomposed by alkalies gives the alloisomeric α-chlorcrotonic acid melting at 98°.

By-product formed in the Addition of Chlorine to Solid Crotonic Acid.

In the preparation of $\alpha\beta$-dichlorbutyric acid mention was made of an oil from which the solid acid separates and which does not solidify further on long standing. A small quantity of the solid addition product may be obtained by allowing the oil to stand in a vacuum over sulphuric acid for a number of days, when it separates in large crystals; the greater part of the oil, however, could not be brought into a solid state. We endeavored to purify this oil, which is an acid, by fractionation in a vacuum, but it decomposed in the operation. A second portion was then treated in alcoholic solution with chlorhydric acid, and the ether thus obtained fractionated in a vacuum. In this manner it was easy to obtain a good yield of a colorless oil that boiled at 93° under 30 mm. pressure (oil-bath 145°–150°). This oil agreed in its properties with $\alpha\beta$-dichlorbutyric ether, but the analyses showed that it contained a small amount of an impurity that could not be separated by fractionation, as the chlorine estimations were from 1.2 to 1.5 per cent. below those indicated by theory. That it consisted largely of $\alpha\beta$-dichlorbutyric ether was further confirmed by its behavior toward alkalies. Six grams oil were treated with alcoholic potash and the mixture allowed to stand for several hours. The precipitate was dissolved in water, acidified, and the solution extracted with ether. On evaporation of the ether, α-chlorcrotonic acid melting at 97°–98° was obtained. The alcoholic filtrate was

worked up for chlorcrotonic acid, and was found to contain a very small amount of allo-α-acid melting at 67°.

To judge from these experiments it seems probable that the oil consisted largely of $\alpha\beta$-dichlorbutyric acid which was prevented by some impurity from solidifying.[1]

Remarks on the Preceding Experiments.

The constitutions of two of the three known bromcrotonic acids may be regarded as hardly open to doubt. If, as seems reasonably certain, α-dibrombutyric acid has the constitution generally assigned to it, then α-bromcrotonic acid (106°), obtained from it by elimination of bromhydric acid, can have no other constitution than $CH_3 - CH - CBr - COOH$. In regard to the new acid formed by addition of bromhydric acid to tetrolic acid, it is safe to assume, relying on the rule that the halogen takes the β-position towards carboxyl which is true without any exception,[2] and that chlorhydric acid unites with tetrolic acid to form β-chlorcrotonic acid, that we have in this acid a β-bromcrotonic acid of the constitution $CH_3 - CBr - CH - COOH$. The formation of the third bromcrotonic from $\alpha\beta$-dibrombutyric acid admits of three different interpretations:

$$CH_3\text{-}CHBr\text{-}CHBr\text{-}COOH = \begin{cases} \text{I. } CH_3\text{-}CH\text{-}CBr\text{-}COOH + HBr \\ \text{II. } CH_3\text{-}CBr\text{-}CH\text{-}COOH + HBr \\ \text{III. } CH_2\text{-}CH\text{-}CHBr\text{-}COOH + HBr \end{cases}$$

Of these three formulae those marked as I and II are impossible for the acid, as acids of these constitutions have been obtained by different methods and found to be different from the acid in question. There remains, assuming for the moment the impossibility of two chemical isomerides being represented by the same structural formula, the formula marked III, and we shall briefly consider whether there are any reasons for assigning this constitution to the third acid.

[1] We subsequently succeeded in obtaining $\alpha\beta$-dichlorbutyric acid from this ether. It was gently heated in an open vessel with strong chlorhydric acid for several hours, and the solution extracted with ether. After drying over calcium chloride the ether was evaporated, and the residue placed in a vacuum over sulphuric acid, when it gradually solidified, and the solid substance was found to be identical with $\alpha\beta$-dichlorbutyric acid.

[2] According to Hemilian (Annalen der Chemie **174**, 326), hydriodic and bromhydric acids form principally α-addition products besides small quantities of β-acids. This view is based on a misconception of the behavior of β-halogen acids towards reagents, and, as we shall show in another paper, the relative proportions of α- and β-acids formed in the reaction should be reversed.

The influence of carboxyl on the hydrogen of an organic acid shows itself primarily on those of the adjacent carbon in making these hydrogen more reactive, or, in other words, loosening its affinity to carbon. This is the reason why the α-hydrogen of an acid are those that enter into chemical reactions in preference to the hydrogen of the following carbons, and that β-halogen acids decompose with such great facility into unsaturated acids and halhydric acids, in contradistinction to the behavior of α-derivatives, that, owing to the greater affinity of hydrogen for carbon in the β-position, decompose with difficulty, and generally form substitution products instead of unsaturated acids. While it is safe to follow the relation between chemical structure and properties as indicated by the present structural formulae as far as hydrocarbon radicals in the α- and β-position towards carboxyl are concerned, any assumption in regard to the relation between carboxyl and such radicals in other positions must for the present be regarded as dogmatic, as the present hypotheses do not show this connection further than the β-position. We may assume, however, that carboxyl does not influence in a marked degree the hydrogen of a hydrocarbon radical in the γ-position, as in no case have γ-derivatives been found among the products formed in the action of halogens on such acids, nor have these hydrogen entered in reactions involving condensations or polymerisations. For these reasons it is theoretically improbable that in the formation of the third bromcrotonic acid from $\alpha\beta$-dibrombutyric acid, γ-hydrogen and β-bromine should be those that are eliminated. If we judge from analogous reactions it is α-hydrogen and β-bromine that split off, as $\alpha\beta$-dibrompropionic acid forms α-bromacrylic, and $\alpha\beta$-dibromhydrocinnamic forms two alloisomeric α-bromcinnamic acids under the same conditions. We believe that the only probable structural formula for the third bromcrotonic acid is that already assigned to α-bromcrotonic acid, and, to distinguish it from that compound, we have called it allo-alpha-bromcrotonic acid, a name indicating that the acid is the α-derivative of allocrotonic acid. It is particularly the remarkable differences noticed in decomposing $\alpha\beta$-dibrombutyric acid and its ethyl ether that show the improbability of the third acid having the constitution $CH_3 - CH - CHBr - COOH$. We can hardly imagine that the ether should lose β-halogen and α-hydrogen, as has been shown by the formation of α-bromcrotonic acid from it, while the free acid should not lose halogen and

hydrogen in a similar manner.[1] These are in fact reactions that show how totally inadequate the present hypotheses are to explain or represent the formation of alloisomeric compounds.

These views apply with equal force to the constitution of the chloro-crotonic acids. The formation of α-chlorcrotonic acid (98°) from $\alpha\beta$-dichlorbutyric ether proves that this acid corresponds in its constitution to the α-bromcrotonic acid (106°) obtained from $\alpha\beta$-dibrombutyric ether and α-dibrombutyric acid, and the new chlorcrotonic acid can have no other constitution than that of an $\alpha\lambda$-α-chlorcrotonic acid, represented by the same structural formula as the α-chlorcrotonic acid.

It is unnecessary to make more than a brief mention of the improbability of β-chlorallocrotonic acid having the constitution $CH_2 - CCl - CH_2 - COOH$. This view assumes the elimination of γ-hydrogen, which directly contradicts everything that is known regarding the influence of carboxyl on the hydrogen of organic acids. The formation of two acids in the action of phosphorus pentachloride on acetacetic ether possibly stands in connection with the formation of different halogen-crotonic acids from an ether or the free acid. One of the chlorcrotonic acids may be formed by elimination of chlorhydric acid from the chloride of β-dichlorbutyric acid, when the second acid is formed from the ether of that acid.[2]

In view of the results described in this paper, as well as in our papers on the bromcinnamic acids, it is necessary to change the law on the decomposition of $\alpha\beta$-halogen acids as stated by Erlenmeyer.[3] According to that chemist, α-halogen and β-hydrogen are principally eliminated, but a secondary reaction takes place, in which β-halogen and α-hydrogen are split off. This law cannot be longer upheld, and must be modified to read that when two halogen acids are formed in the decomposition of an $\alpha\beta$-dihalogen acid, both these products are α-derivatives of alloisomeric acids, and when but one acid is formed, the acid is an α-derivative.

TUFTS COLLEGE, MASS.

[1] It is probable that the tribrombutyric acids obtained from α- and $\alpha\lambda$-α-bromcrotonic acid by addition of bromine are identical. We intend to repeat these experiments, and also to make a thorough examination of the brom- and chlorcrotonic acids with a view of bringing further proofs of the constitutions of the compounds presented in this paper.

[2] We intend to make a thorough comparative examination of the behavior of halogen acids and their ethers towards alkalies, to ascertain whether the differences that were observed between dibrombutyric, hydrocinnamic, and dichlorbutyric acids and their ethers towards alkalies represent a general law. This investigation promises to open a very interesting field of research, and we should like to reserve the continuation of our observations on this subject until the work is completed.

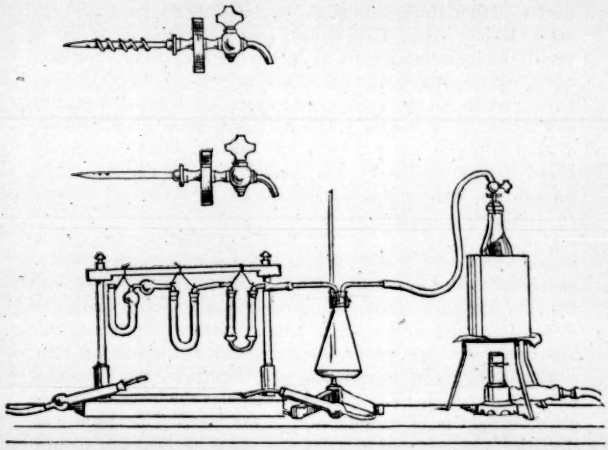
[3] Berichte d. deutsch. chem. Gesell. 15, 49.

Contributions from the Laboratory of the U. S. Department of Agriculture.

X.—THE ESTIMATION OF CARBONIC ACID IN BEER.

By C. A. Crampton and T. C. Trescot.

Most analysts have given very little attention to the determination of the carbonic acid in malt liquors, regarding it as of but little importance in forming an estimate of the quality of the sample examined. The practical consumer, however, is of quite a different opinion, and condemns immediately a beer which is "flat" or insufficiently carbonated, however worthy it may be in other respects. The reason for its importance as a determination is found in the difficulty of its accurate estimation in the beer as supplied to the consumer. The usual method of determining it is to measure or weigh out a convenient quantity of the beer into a flask, connect the latter either with an absorbing apparatus for the estimation of the carbonic acid direct, or with a suitable apparatus for the retention of watery vapor, thus estimating it by loss, or indirectly; its liberation being accomplished in either case by a low degree of heat. But this manner of manipulation gives simply the amount of carbonic acid capable of being held in solution by a liquid of the density and temperature of the beer when it was measured out, supposing it to have been fully charged previously. The excess of gas above the saturation point, however, which is held by the beer so long as it is kept under pressure or at a low temperature, escapes as soon as the pressure is removed, and gives the beer its "head," which is so desirable a qualification. This excess of gas soon passes off after it is drawn from a cask, or a bottle opened, but in this short interval the beer is drank. The problem is to estimate the carbonic acid just as it exists in the beer before consumption. This is a difficult matter with beer contained in casks or kegs, though it might be accomplished by drawing a sample off by means of gas-tight connections, as in gas analysis. But where the beer is furnished in stoppered bottles it is an easy matter, and furnishes a most valuable index as to the freshness and proper preparation of the beer. Where secondary fermentation or souring has set in there will be an excess of carbonic acid, and the beer will have become turbid. Where there is a good content of carbonic acid, but the acidity of the beer is very low, the indications are that bicarbonate of soda has been added.



In the course of an investigation of the composition and extent of adulteration of the beers sold in this country we had occasion to devise a form of apparatus to accomplish this purpose. Hassall speaks of the estimation of carbonic acid in bottled aerated waters, the gas being drawn by means of a champagne tap, and Dr. Wiley[1] has estimated the carbonic acid in koumiss in that way, using a calcium chloride tube for the retention of the water carried off by the gas, and estimating it by difference, the whole bottle being weighed. In applying this form of apparatus to beer we experienced considerable difficulty on account of the viscosity of the liquid. The bubbles formed were so tenacious that when the bottle was connected directly with a calcium chloride or sulphuric acid tube, the latter would become filled with the beer in a very short time. This difficulty was obviated by the use of the form of apparatus shown in the cut. The cork of the bottle is pierced with a champagne tap, and this is connected with an Erlenmeyer flask, in the broad bottom of which the bubbles are broken and not allowed to pass beyond it; next comes a U-tube filled with sulphuric acid,

[1] This Journal **8**, 200; Ann. Rept. U. S. Dept. Agr. 1886, 118.

then a calcium chloride tube, then a soda-lime tube to absorb the dried carbonic acid. The bottle of beer is placed in a convenient vessel—an empty ether can with the top cut off answers admirably, as in the cut—which is nearly filled with cold water. After the apparatus is connected the tap is opened slowly and the gas allowed to flow through the apparatus. When it ceases to flow spontaneously, a lamp is placed under the can and the temperature gradually raised until it reaches 80° C., beyond which it should not be carried. By keeping it at this temperature for about half an hour and taking the bottle out and shaking it occasionally, all the carbonic acid may be driven off. Then the tube from a suction pump is connected with a calcium chloride tube, and this in turn with the soda-lime tube. The valve of the tap is then closed, the latter removed from the bottle, connected with a soda-lime tube, and by gradually opening the valve a stream of air from which the carbonic acid has been removed is drawn through the apparatus by the pump, so that all the carbonic acid contained in it is drawn into the soda-lime tube and absorbed. The increase in weight of the latter, of course, gives the amount of carbonic acid in the beer. The quantity of the latter is measured or weighed, that which has been carried into the Erlenmeyer flask being added. In the case of large bottles it may be found necessary to add a second soda-lime tube, and it is best to use fresh soda lime for each determination. It was found necessary to modify the champagne taps used, for the thin-edged thread with which they are provided cuts the cork too much and allows the escape of the gas. Accordingly this thread was turned off entirely, leaving a smooth tube, as shown in the accompanying figures. This can be forced through the cork with little difficulty, and allows no leakage of gas. It was also found necessary to have the cock reground to make it fit accurately.

The patent rubber-stoppered beer bottles presented a difficulty in this method of analysis, as it was impossible to make a gas-tight connection with them without the escape of the confined gas. In these the gas was estimated by loss in weight, calcium chloride and sulphuric acid tubes and connections being weighed with the bottle on a large balance, the bottle opened and connections made as soon as possible, the gas driven off as before, and the loss ascertained by weighing the entire apparatus again. It is necessary to raise the heat very gradually to prevent the filling up of the tubes with the beer carried over by the bubbles. There is a slight error from

the watery vapor which escapes with the pressure of gas when the bottle is opened, and altogether the determination is not so satisfactory as with the cork-stoppered bottles. Analyses of bottled beers made in this way gave much higher results than are given in the books, as the following table shows.

No.	Per cent. CO_2.	No.	Per cent. CO_2.
1	.411	10	.629
2	.300	11	.344
3	.489	12	.503
4	.415	13	.397
5	.328	14	.441
6	.471	15	.592
7	.717	16	.242
8	.219	17	.265
9	.324		

Nos. 1, 3, 4 and 7 had rubber stoppers, the rest cork. No. 7 was evidently in a state of after fermentation, cloudy and acid; excluding that analysis, the 16 others give an average of .398 per cent.; most authorities give an average of .1 to .2 per cent. in beer.

In Nos. 2 and 5 duplicate analyses were made with different bottles of the same lot, with the following results:

	I.	II.
No. 2	.294	.307
No. 5	.329	.327

A sample of bottled cider which had evidently been manufactured, as shown by other tests, gave in different bottles the following numbers:

I.	II.	III.
.728	.654	.482

Bicarbonate of soda had probably been added to each bottle in varying amount. It is likely that in all cases of bottled ciders where the content of carbonic acid is very high, that it has been added to the cider in some way, for cider that has been racked and cleared, fit for bottling, contains very little carbonic acid, barely enough to give it a slight sparkle. This is a matter for further investigation. Two samples of "champagne cider" analysed by us gave the following per cent. of CO_2: .161, .120.

AN IMPROVED FORM OF ELLIOTT'S GAS APPARATUS.

By J. B. Mackintosh.

In the ordinary form of this apparatus as described by Elliott,[1] the transfer of the residual gases from the absorption apparatus to the explosion burette is attended with some difficulty and with the liability of accidentally introducing some air during the operation unless great care be taken. In order to obviate these troubles and, incidentally, also to diminish the number of loose pieces, I have devised the simple modification shown in the illustration. The essential feature is the three-way T-stopcock on the measuring burette, whereby connection may be made between any two of the burettes, to the complete isolation of the other. Another time-saving device is in the fixing of the zero points of the graduations. In the measuring and explosion burettes the zero point *O* is taken at that point where the capillary tube expands into the burette, and where the water will naturally remain when the excess drains to the bottom of the burette. This renders the adjustment to zero an automatic one, with no sacrifice of accuracy. The absorption tube has a single graduation at 100 cc. measured from the point *A*. In filling this tube with gas to the mark, a small quantity remains in the portion of the tube above *A*, but this may be removed by first closing the lower stopcock *S* and then forcing water out of one of the other burettes. This slightly compresses the gas in the absorption tube, and at the same time expels the excess, so that we then have exactly 100 cc. at the atmospheric pressure.

In transferring gas to the explosion burette from the measuring tube, the portion remaining in the capillary tube and in the ways of the T-stopcock is removed by passing water from the absorption tube, preferably by letting it flow in from the funnel. The T-stopcock being then turned so as to connect the explosion and absorption tubes, the gas remaining in the measuring tube is perfectly isolated, and none of it has been lost during the transfer. We are now ready to introduce oxygen and air for the explosion, which may be done either as Elliott directs, through the lower stopcock of the explosion burette, or through the funnel of the absorption tube, or both.

[1] School of Mines Quarterly **3**, 16, and **4**, 322; and Chemical News, October, 1883.

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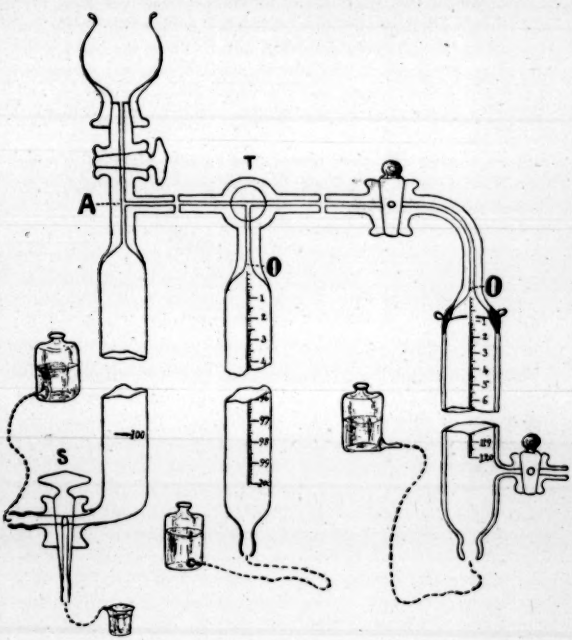

In case we have not a store of oxygen under pressure for use, I have found that a very convenient source of this indispensable reagent is available in the reaction of peroxide of hydrogen on acidified solution of potassium permanganate. We can thus manufacture in the absorption tube as much pure oxygen as we need, by first running in some permanganate, then the peroxide of hydrogen, and then more permanganate, until we have added enough to decompose all the peroxide taken. We then wash the permanganate out of the funnel, etc., with water, pass as much oxygen as we need into the explosion burette, empty the capillary tube of oxygen as before by letting water run in from the funnel, and, finally, empty and wash out the absorption tube and make it

in readiness for the absorption of the carbonic acid resulting from explosion. Air may now be introduced in sufficient quantity, and after mixing the gases by removing and inclining the burette, the explosion may be made, the contraction noted, the gas transferred to the absorption burette, and the carbonic acid absorbed, and, finally, retransferred to the explosion burette and the residual gas measured.

The apparatus as figured was made for me by Mr. Emil Greiner of 79 Nassau Street, New York, to whose good workmanship I am pleased to render tribute.

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A NEW PYROMETER.

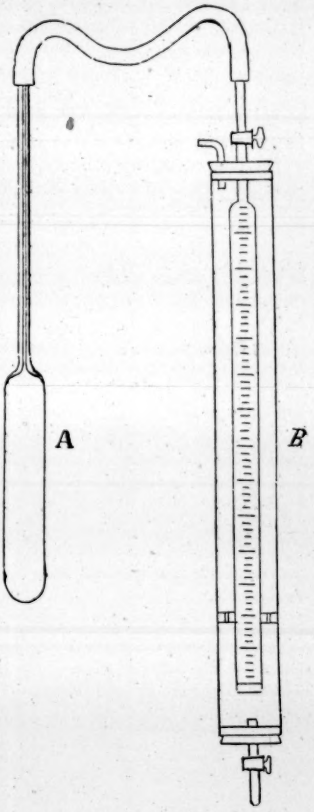
BY E. H. KEISER.

New methods for the determination of high temperatures have recently been described by Justus Mensching and Victor Meyer,[1] and by L. F. Nilson and Otto Pettersson.[2] In both cases the apparatus is constructed for the double purpose of measuring high temperatures and making vapor density determinations. Excellent as these methods are, a single temperature determination by either one of them requires the employment of a complicated system of apparatus, and must undoubtedly take considerable time. In chemical laboratories it is, however, frequently necessary to determine melting and boiling points which lie above 360° C. It is therefore very desirable to have a simple form of air thermometer by means of which these high temperatures may be rapidly and accurately determined. The following is a description of an apparatus which fulfills these conditions and which has given satisfactory results in my laboratory.

The pyrometer consists of two parts, the bulb *A* and the eudiometer *B*. The vessel *A* has a capacity of about 100 cubic centimeters. It is closed at one end, and to the other end is attached a capillary stem which is from 20 to 25 centimeters in length. For measuring temperatures below the melting point of glass this bulb may be made of hard glass. For higher temperatures it may be made of wrought iron, porcelain, or platinum, according to the

[1] Zeitschrift für physikalische Chemie **1**, 145. [2] Journal für praktische Chemie **33**, 1.

intensity of the heat which it is desired to measure. The eudiometer *B* consists of a graduated tube which is open at the bottom and is provided with a stopcock at the top. It is surrounded by a glass water-jacket. By means of the stopcock at the bottom of the water-jacket and the tube which passes through the stopper at the top, water may be easily poured into or allowed to flow out of the outer glass cylinder. Gases which collect in the eudiometer may be rapidly put under atmospheric pressure and their volumes determined with great accuracy by means of this apparatus. A short piece of rubber tubing of small diameter and thick walls is used to connect the bulb *A* with the eudiometer *B*.



To determine the temperature of any substance with this instrument it is necessary to bring the level of the water on the outside and inside of the eudiometer to the zero point. Then if both *A* and *B* have acquired the temperature of the surrounding air they are connected by means of the rubber tubing. A definite volume of air under atmospheric pressure will now be contained in the bulb *A* and the tube which connects the bulb with the eudiometer. The temperature of the air confined in the apparatus is the same as that of the room in which the instrument is placed ;

it is read off on a thermometer attached to B. The bulb A is then introduced into the heated substance. Air will be driven out of the bulb into the eudiometer. When the volume of gas in B no longer increases, water is allowed to flow out of the stopcock at the bottom of the water-jacket until the level of the liquid is the same on the outside and inside of the eudiometer. The volume of air in the eudiometer is then read off on the graduated tube.

The temperature to which the bulb has been raised may now be readily calculated by means of the formula

$$t' = t + \frac{V}{C - \frac{V}{273 + t}}$$

in which $t' =$ the desired temperature expressed in degrees centigrade; $t =$ the temperature of the room and eudiometer;[1] $V =$ the volume of air measured in the eudiometer under atmospheric pressure, and $C =$ a constant for any given temperature t. It depends upon the capacity of the bulb A and upon the coefficients of expansion of air, and of the material of the bulb at the temperature t.

The value of the quantity C may be easily determined by placing the bulb in steam, or any other vapor of known temperature, and measuring the volume of gas driven over into the eudiometer. Then by substituting the known quantities in the formula the equation may be solved for C.

The following temperature determinations were made with an apparatus the bulb of which had a capacity of about 60 cubic centimeters.

I.

Temperature of the room and pyrometer $= 24°$. In order to determine the value of C the bulb was plunged into steam. The volume of gas in the eudiometer (V) measured 9.6 cubic centimeters.

$$100 = 24 + \frac{9.6}{C - \frac{9.6}{297}},$$

$$C = .1586.$$

After the bulb had cooled down to the temperature of the room, and the level of the water in the eudiometer had been adjusted so

[1] As only a very short time is required for a determination, the temperature of the eudiometer does not change appreciably. It is well, however, to protect the connecting tube and the eudiometer from the rays of heat by an asbestos or a wooden screen.

that it stood at the zero point, the air bulb was introduced into the vapor of boiling nitro-benzene.

Volume of gas expelled, $V = 18.2$ cc.

$$t = 24°,$$

$$t' = 24 + \frac{18.2}{.1586 - \frac{18.2}{297}} = 211°.$$

II.

Temperature of room and pyrometer $= 24°$. Volume of air expelled from the bulb by the vapor of boiling diphenylamine, $V = 22.7$ cc.; $t' = 300°$.

III.

Temperature of room and pyrometer $= 24°$. Volume of air expelled from the bulb by the vapor of boiling sulphur, $V = 27.5$ cc.; $t' = 440.7°$.

BRYN MAWR, PA., *May*, 1887.

Contributions from the Sheffield Laboratory of Yale College.

XXVII.—BASIC LEAD NITRATES.

BY A. J. WAKEMAN AND H. L. WELLS.

The basic nitrates of lead have been investigated by a number of chemists. The existence of diplumbic nitrate, $Pb(NO_3)OH$, has been well established and frequently confirmed. In addition to this, a number of more basic salts have been described, but with quite discordant results, and some of these, made by precipitation with an alkali and not recrystallised, are open to doubt. The object of this investigation was to clear up the doubt concerning these more basic salts.

Berzelius obtained a salt to which he gave a composition corresponding to the formula $2(3PbO.N_2O_5).3H_2O$. The composition of this salt was afterwards confirmed by Meissner.[1] Volge[2] obtained a salt differing from that of Berzelius in containing double the number of water molecules. The most extended investigations of the subject, however, have been made by Löwe and Morawski. Löwe[3] describes two basic salts, the one a

[1] Jahresber. Fort. d. Chem. 1876, 194. [2] Ann. d. Chem. u. Pharm. **94**, 96.
[3] Jour. prakt. Chem. 1866, 388.

triplumbic nitrate having the formula $6PbO.2N_2O_5.2H_2O$, the other a salt having this formula less one molecule of water. Morawski[1] obtained a yet more basic salt to which he gave the formula $10PbO.3N_2O_5.5H_2O$. This and the second salt of Löwe were afterwards confirmed by Smolka.[2] The following is a summary of formulæ arrived at by the above named investigators:

Berzelius,	$6PbO.2N_2O_5.3H_2O$.
Meissner,	$6PbO.2N_2O_5.3H_2O$. or $6PbO.2N_2O_5.H_2O$.
Volge,	$6PbO.2N_2O_5.6H_2O$.
Löwe,	$6PbO.2N_2O_5.2H_2O$. or $6PbO.2N_2O_5.H_2O$.
Morawski,	$10PbO.3N_2O_5.5H_2O$.
Smolka,	$6PbO.2N_2O_5.H_2O$. or $10PbO.3N_2O_5.5H_2O$.

From this table it is seen, therefore, that all the salts, with the exception of Morawski's and one of Smolka's, agree in the ratio of the lead oxide to the nitric acid, 3 : 1, the difference occurring in the amount of water they contain. The method of analysis in some cases, however, as in that of Löwe, was questionable, the water being determined by drying, and the nitric acid by difference. In the present investigation, complete analyses have been made in every case, and, moreover, each product has been subjected to microscopic examination, and many which were mixtures were rejected. The salts were dried in each case over concentrated sulphuric acid, and special care was taken to avoid contact with carbonic acid.

The diplumbic nitrate was made in the first place, and the result of previous investigators was confirmed. This salt was found to possess a double crystalline form; both flat scale-like crystals and prismatic crystals frequently separated from the same solution. The scaly crystals showed a mono- or triclinic habit, strong double refraction, brilliant polarisation colors, and an extinction angle of fourteen degrees. The prismatic crystals were too small and ill-defined to be studied with any degree of accuracy. No crystals were obtained sufficiently large for measurement. The following are results of analyses:

[1] Jour. prakt. Chem. 1880, 414.

[2] Monatsh. f. Chem. 1885, 195.

	Scaly crystals.		Mostly prismatic.			Calculated for $Pb(NO_3)OH$.
	I.	II.	III.	IV.	V.	
PbO	77.39	77.41	77.04	76.69	78.37	77.96
N_2O_5	19.14	18.82	18.54	20.01	18.54	18.89
H_2O	3.51	3.68	3.56	3.20	3.27	3.15
	100.04	99.91	99.14	99.90	100.18	100.00

Repeated attempts were made to obtain the triplumbic nitrates, but in each case a single salt of different formula resulted. Following the directions given in Roscoe and Schorlemmer,[1] ammonia was added to a solution of normal lead nitrate in slight excess. A white powdery precipitate formed. The solution was boiled with addition of some of the normal nitrate until the odor of ammonia had nearly disappeared, and filtered while hot. A crystalline product separated from the filtrate while cooling. This was recrystallised. The crystals were flat tabular in shape, and of triclinic habit, with extinction angle of about thirty-five degrees. They showed an optical axis in convergent light, and gave a strong interference figure. They were too small, however, to be measured. The salt was found to be less soluble in water than the diplumbic nitrate. It was stable, undergoing no decomposition in boiling water nor by repeated crystallisation. The same salt resulted under varying conditions of concentration. The following are results of analyses of five separate samples of the salt, number II being the fourth recrystallisation of number I:

	I.	II.	III.	IV.	V.
PbO	84.82	84.79	84.75	84.95	83.66
N_2O_5	12.32	12.23	12.27	12.53	12.90
H_2O	2.61	2.81	2.64	2.65	2.94
	99.75	99.83	99.66	100.13	99.50

	Calculated for $10PbO.3N_2O_5.4H_2O$.	Calculated for $3PbO.N_2O_5.H_2O$. (Formula of Löwe and others.)
PbO	84.92	84.14
N_2O_5	12.34	13.60
H_2O	2.74	2.26
	100.00	100.00

Next, a large excess of ammonia was employed instead of a

[1] Vol. 2, Pt. I, p. 289.

slight excess as before, using different conditions of concentration and length of time of digesting with ammonia. The resulting salt crystallised in small crystals of triclinic habit resembling those already described. The following results of analyses were obtained on three separate products:

	I.	II.	III.
PbO	84.83	84.87	84.81
N_2O_5	12.10	12.43	12.17
H_2O	2.60	2.56	2.63
	99.53	99.86	99.61

These results agree closely with those just preceding, and show, therefore, that the salts are identical.

When a very small amount of ammonia was employed, not an excess, the resulting product was the diplumbic nitrate.

From these data, therefore, it may be safe to draw the conclusion that, in the formation of basic lead nitrates by means of ammonia, only one salt capable of recrystallisation results by the use of either a slight or a large excess of the alkali.

In the examination of the salts resulting from the use of ammonia, some difficulty was experienced from the fact that diplumbic nitrate was frequently mixed with the more basic salt, as was shown by microscopic examination; such products were rejected.

Morawski[1] obtained a basic lead nitrate from his so-called plumbonitratoglyceride by decomposing the same in boiling water. This salt he calls a "pentaplumbic" nitrate, and gives to it the formula $10PbO.3N_2O_5.5H_2O$, as before stated. This formula differs from that of the salt just described only by a single water molecule. Accordingly, Morawski's experiment was repeated according to his directions, and the product recrystallised. Analyses of three consecutive crystallisations of the salt are as follows:

	I.	II.	III.
PbO	84.30	84.69	84.86
N_2O_5	12.34	12.93	12.11
H_2O	3.12	2.96	3.17
	99.76	100.58	100.14

This points clearly to the formula $10PbO.3N_2O_5.4H_2O$; showing, therefore, that Morawski's salt is identical with the salt under

[1] Loc. cit.

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consideration. It would seem, besides, from the average results of five analyses made by Morawski, that the formula $10PbO.3N_2O_5.4H_2O$ is indicated, rather than the one he assigned to the salt. Thus:

	Calculated for $10PbO.3N_2O_5.5H_2O$. (Morawski.)	Morawski's average of results.	Calculated for $10PbO.3N_2O_5.4H_2O$. (Wakeman and Wells.)
PbO	84.34	84.74	84.92
N_2O_5	12.25	11.88	12.34
H_2O	3.41	2.77	2.74
	100.00	99.39	100.00

Investigation was also made of Löwe's salt. He obtained his so-called triplumbic nitrate by precipitating in a basic lead acetate solution with potassium nitrate. He arrived at two formulæ: $3PbO.N_2O_5.H_2O$ and $2(3PbO.N_2O_5).H_2O$. The salt, made according to his method, was twice recrystallised, the crystals separating in little tufts, and resembling Morawski's salt in crystalline habit. Upon analysis they gave the following results:

	I.	II.
PbO	84.68	84.53
N_2O_5	12.41	12.41
H_2O	2.93	3.14
	100.02	100.08

To Löwe's salt, therefore, belongs the same formula,

$$10PbO.3N_2O_5.4H_2O.$$

Thus the investigation of the basic nitrates of lead has resulted in the establishment of but a single recrystallisable salt besides the diplumbic nitrate.

The method devised by one of us[1] for the analysis of basic cupric nitrates has been employed in the analyses given in this article.

Our thanks are due to Mr. S. L. Penfield, who has given us much advice and assistance in the microscopic examination of our products.

[1] Wells and Penfield, Amer. Jour. of Science [III] **30**, 50.

XXVIII.—BASIC ZINC AND CADMIUM NITRATES.

By Horace L. Wells.

Klinger[1] has described a basic cadmium nitrate to which he gives the formula $Cd\langle^{NO_3}_{OH}.H_2O$. He made this salt, together with basic lead nitrate, by adding lead hydroxide to a hot cadmium nitrate solution, filtering and cooling; also by heating normal cadmium nitrate, and, more easily, by dissolving cadmium hydroxide in hot cadmium nitrate solution, when the salt crystallised out on cooling. His salt was freed from normal nitrate by washing with alcohol.

I have confirmed Klinger's result[2] as follows: Cadmium oxide was added to a hot concentrated solution of normal cadmium nitrate as long as it continued to dissolve, the liquid was filtered hot, and, upon cooling, a good crop of very thin scaly crystals separated; they were collected on a filter, washed thoroughly with absolute alcohol and dried over sulphuric acid. When dry they had a pure white color and possessed a beautiful pearly lustre, as is usual with very thin crystals. Analysis gave the following results:

	Found.	Calculated for $N_2O_5.2CdO.3H_2O$.
N_2O_5	26.01	25.83
CdO	60.99	61.25
H_2O	13.08	12.92
	100.08	100.00

Since no zinc nitrate has been described corresponding to this cadmium salt, and since, as far as I know, indeed, none has been made which has been washed with alcohol to avoid decomposition with water, a basic zinc nitrate was made in exactly the same manner as the cadmium salt, by the use of concentrated zinc nitrate solution and zinc oxide. It was carefully washed with absolute alcohol and dried over sulphuric acid. The salt was obtained in

[1] Berichte d. deutsch. chem. Gesell. **16**, 997.

[2] The figures given in Klinger's article do not agree with his formula; he gives:

	"Gefunden.	Berechnet.
CdO,	61.28, 61.11	61.17
H_2O,	8.52	8.63."

These figures would give the formula $4N_2O_5.7CdO.7H_2O$ instead of $N_2O_5.2CdO.3H_2O$. Since my results agree with his formula, I conclude that there is a mistake in his published figures.

very slender prismatic crystals, entirely different in appearance from the cadmium compound. When dry it appeared and felt much like a mass of cotton. It was analysed with the following results:

	Found.	Calculated for $N_2O_5.2ZnO.3H_2O$.
N_2O_5	33.43	33.33
ZnO	50.07	50.00
H_2O	17.16	16.67
	100.66	100.00

Thus it is seen that the basic nitrates of zinc and cadmium, as might be expected, correspond exactly in composition.

These two salts are very readily decomposed by water; even ordinary strong alcohol decomposes them slowly. A sample of the cadmium salt washed once with cold water with a suction pump gave on analysis:

		Ratio.
N_2O_5	22.93	1.
CdO	64.34	2.38
H_2O	12.93	3.38
	100.24	

The fact that some normal nitrate probably remained in this product shows how readily it is decomposed by water.

Several samples of both salts were made and washed with water under varying conditions, in order to study the decomposition and to decide if any definite basic nitrate could be thus made.

The following are analyses of separate samples washed with cold water with a suction pump not much more than enough to remove the normal nitrate. They were all dried over sulphuric acid.

From zinc salt:

	A.		*B.*	
		Ratio.		Ratio.
N_2O_5	17.42	1.	15.00	1.
ZnO	65.11	5.	67.09	5.94
H_2O	17.45	6.	17.75	7.10
	99.98		99.84	

From cadmium salt:

	A.	Ratio.	*B.*	Ratio.	*C.*	Ratio.
N_2O_5	12.35	1.	12.38	1.	11.75	1.
CdO	74.34	5.06	74.81	5.09	75.36	5.40
H_2O	13.46	6.50	12.88	6.22	12.77	6.50
	100.20		100.07		99.88	

The following were washed excessively with *cold* water and dried over sulphuric acid.

From zinc salt:

		Ratio.
N_2O_5	15.45	1.
ZnO	66.43	5.73
H_2O	18.01	6.22
	99.89	

From cadmium salt:

		Ratio.
N_2O_5	7.53	1.
CdO	79.36	9.
H_2O	12.51	10.
	99.40	

The following were thoroughly washed with *hot* water and dried over sulphuric acid.

From zinc salt:

		Ratio.
N_2O_5	0.20	...
ZnO	97.40	10.
H_2O	2.22	1.
	99.81	

From cadmium salt:

		Ratio.
N_2O_5	0.30	...
CdO	86.60	1.
H_2O	12.16	1.
	99.06	

It appears from the above results that the cadmium salt is decomposed to a greater extent by cold water than the zinc salt. It seems also that, after a certain amount of decomposition has

taken place, further change, particularly in the case of the zinc salt, takes place very slowly, if at all; this indicates the possibility of the existence of more basic nitrates, perhaps $N_2O_5.5ZnO.6H_2O$ or $N_2O_5.6ZnO.7H_2O$, and the corresponding cadmium compounds. It is to be noticed, however, that if the ratio $N_2O_5 : ZnO$ or $CdO : H_2O = 1 : 2 : 3$ be subtracted from the ratios found for the products washed with cold water, the remainder is always close to ZnO or $CdO : H_2O = 1 : 1$; hence all these products may be regarded as mixtures of the 1 : 2 : 3 nitrates with different amounts of the hydroxides. Even if it is necessary to assume that more basic nitrates exist, it would be difficult to decide upon their composition, since the products are wholly amorphous, and there is no means for deciding how much hydroxide is mixed with them, or whether they do not contain more than one basic nitrate.

It is an interesting fact, brought out by the last two analyses, that by washing with hot water the cadmium salt leaves the hydroxide, while the zinc salt leaves the almost pure oxide as a residue.

Previous investigators of basic zinc or cadmium nitrates, with the exception of Klinger, whose work is referred to at the beginning of this article, have apparently washed their products with water, or experimented in a still more uncertain way by heating the normal nitrate and analysing the residue which happened to be left. The following is a summary of the previous results as far as I have been able to find them. The formulæ have been transformed for the sake of easy comparison, and have been translated into the new system when necessary.

Grouvelle[1] was the first investigator of basic zinc nitrates. He formed it by heating the normal nitrate, $N_2O_5.8ZnO.2H_2O$, and by adding a small quantity of ammonia to a solution of the normal nitrate, $N_2O_5.8ZnO.4H_2O$.

Schindler[2] made $N_2O_5.8ZnO.2H_2O$ in the same way as Grouvelle, thus confirming the latter's result; he made also $N_2O_5.4ZnO.2H_2O$ by boiling the first compound with solution of the normal nitrate.

Ordway[3] analysed the mass left by heating normal zinc nitrate and obtained $N_2O_5.4ZnO.3H_2O$.

[1] Ann. de Chim. et de Phys. 1821 [2] **19**, 137.

[2] Gmelin's Handbook, London Ed. **5**, 34; Würtz Dict. de Chim.; Watts' Dictionary. Reference to original article could not be found.

[3] Am. Jour. Sci. [2] **32**, 14.

Gerhardt[1] also made $N_2O_5.4ZnO.3H_2O$, in prismatic needles. I have been unable to consult his original article[2] and do not know how this was prepared.

Bertels[3] showed that the vitreous mass obtained by Ordway has not a constant composition, but by treating this mass with water he obtained $4N_2O_5.7ZnO.14H_2O$. This is quite close to my formula, $N_2O_5.2ZnO.3H_2O$; he could not have washed this much with water. Bertels obtained also $N_2O_5.6ZnO.8H_2O$ by treating an excess of metallic zinc with nitric acid.

Habermann[4] made $N_2O_5.5ZnO.5\frac{1}{2}H_2O$ by treating normal zinc nitrate solution with ammonia as long as a precipitate formed, and washing the product with water; in the same manner he obtained from cadmium nitrate solution $N_2O_5.12CdO.11H_2O$.

It seems probable that all the above compounds, except Ordway's and the first of Bertels, are decomposition products made by washing the 1 : 2 : 3 basic nitrate with water. The fact that several of them have less water than I have found in such products can be explained if it is supposed that they were dried at 100°; for I have found that the zinc product which gave a ratio 1 : 5 : 6 (*A* above) slowly lost a weight corresponding to about one-half of its water when so heated.

In conclusion it may be suggested that all basic nitrates of zinc and cadmium, except the 1 : 2 : 3 salts, be rejected until, by more positive evidence, their existence is established.

[1] Jahresbericht, 1847–8, 436.
[2] J. Pharm. [3] **12**, 61.
[3] Jahresbericht, 1874, 274.
[4] Monatsh. für Chem. 1884, **5**, 447.

NOTES.

The Discovery of Diamide or Hydrazine.

In the course of an investigation on glycine, $CH_2\begin{cases}NH_2\\COOH\end{cases}$, Theodore Curtius found in 1883[1] that by the action of sodium nitrite on the hydrochloride of the ethyl ether of glycine a diazo-compound, $CH.N_2.COOC_2H_5$, is formed. The following formulas illustrate the formation of this compound:

I. $\begin{matrix}CH_2NH_2.HCl\\|\\COOC_2H_5\\\text{Hydrochloride of the Ether.}\end{matrix} + NOONa = \begin{matrix}CH_2NH_2.NO.OH\\|\\COOC_2H_5.\\\text{Nitrite of the Ether.}\end{matrix} + NaCl$

II. $\begin{matrix}CH_2NH_2.NO.OH\\|\\COOC_2H_5\end{matrix} - H_2O = \begin{matrix}CH_2.N_2.OH\\|\\COOC_2H_5.\\\text{Diazoacetic Ether.}\end{matrix}$

III. $\begin{matrix}CH_2.N_2.OH\\|\\COOC_2H_5\end{matrix} - H_2O = \begin{matrix}CH\overset{\diagup N}{\underset{\diagdown N}{\|}}\\|\\COOC_2H_5.\\\text{Compound obtained.}\end{matrix}$

Further investigations have shown that this compound is in all probability a diazoacetic ether, that is, acetic ether in which two hydrogen atoms of the methyl group are substituted by a double atom of trivalent nitrogen ($-N=N-$).

In order to test his hypothesis, Curtius prepared the nitrite of the ethyl ether of glycine, and obtained directly from it the diazo-acetic ether by loss of two molecules of water.[2]

The difference between the constitution of the diazoacetic ether and the hypothetical diazobenzene is expressed by the following formulas:

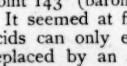
I. $\begin{matrix}CH\overset{\diagup N}{\underset{\diagdown N}{\|}}\\|\\COOC_2H_5.\\\text{Diazoacetic Ether.}\end{matrix}$ II. $\begin{matrix}CH_2-N=N-OH\\|\\COOC_2H_5.\\\text{Hypothetical Diazoacetic Ether (analogous to the hypothetical diazobenzene.)}\end{matrix}$

In I the two free affinities of the double atom of nitrogen saturate two affinities of the methyl carbon of the acetic acid; in II only one, while the other free affinity is saturated by a hydroxyl. It

[1] Berichte d. deutsch. chem. Gesell. **16**, 754, 2230. [2] Ibid. **17**, 953.

is possible that the remarkable stability of the diazo compounds of the ethers of the fatty series is due to this closer connection of both nitrogen atoms with the carbon of the methyl group of the acetic ether. This stability is so great that the diazoacetic ether can be distilled at ordinary pressure without undergoing decomposition. Diazoacetic ethyl ether has the constant boiling point 143° (barometric pressure = 721 mm.).

It seemed at first probable that diazo compounds of the fatty acids can only exist if the hydroxyl in the carboxyl group is replaced by an alkyl. Curtius, however, has shown that the amido group can substitute efficiently the alkyl. Treating diazoacetic ether with ammonia in watery solution he obtained a compound which he calls diazoacetamid, and to which he gives the formula



Within a few weeks past Curtius has obtained[1] the potassium salt of a new diazo fatty acid by treating diazoacetic ether with hot concentrated caustic potash. He says nothing about the constitution of the new acid, except that it is closely related to the derivatives of pseudo-diazoacetamid. If the golden yellow solution of this new acid is digested for a short time with very dilute sulphuric acid, it loses its color without evolution of nitrogen, and on cooling, colorless, beautiful crystals appear. This substance is the sulphate of the long sought diamide or hydrazine

The free diamide can be obtained by heating its salts with solutions of alkali. It is a gas of great stability, which dissolves very easily in water and turns red litmus paper blue. In a concentrated state it possesses a very peculiar odor which is but little suggestive of ammonia.

Hydrazine possesses strong reducing properties. Its chemical behavior corresponds to that of the substituted hydrazines.

E. A. S.

[1] Berichte d. deutsch. chem. Gesell. **20**, 1632.